United States
Environmental Protection
Agency

Atmospheric Research and Exposure
Assessment Laboratory
Research Triangle Park, NC 27711

December 1993

Research and Development

EPA 600/R-93/235

EPA

Preparation of Lead-Containing Paint and Dust Method Evaluation Materials and Verification of the Preparation Protocol by Round-Robin Analysis

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PREPARATION OF LEAD-CONTAINING PAINT AND DUST METHOD EVALUATION MATERIALS AND VERIFICATION OF THE PREPARATION PROTOCOL BY ROUND-ROBIN ANALYSIS

Prepared by

E. E. Williams
D. A. Binstock
W. F. Gutknecht

Center for Environmental Measurements and Quality Assurance
Research Triangle Institute
Research Triangle Park, North Carolina

EPA Contract No. 68-D1-0009
RTI Project No. 4960-141

Mrs. Sharon Harper, Work Assignment Manager

Atmospheric Research and Exposure Assessment Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC

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The information in this document has been funded wholly or in part by the United States Environmental Protection Agency (USEPA) under EPA Contract No.68-D1-0009 to the Research Triangle Institute. It has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ACKNOWLEDGEMENTS

This document was prepared under the direction of Drs. Joseph J. Breen and Benjamin S. Lim of the Office of Pollution Prevention and Toxics (OPPT), U.S. Environmental Protection Agency (USEPA), Washington, DC, and Mr. Michael E. Beard and Ms. Sharon L. Harper of the Atmospheric Research and Exposure Assessment Laboratory (AREAL), U.S. Environmental Protection Agency, Research Triangle Park, NC.

The authors acknowledge the efforts of statisticians Dr. Larry Myers of the Research Triangle Institute, and Mr. Jack Suggs of AREAL/USEPA, Research Triangle Park, NC.

Special acknowledgement is given to Dr. Joseph Walling, AREAL/USEPA, Research Triangle Park, NC; Dr. Benjamin Lim, OPPT/USEPA, Washington, DC; and Dr. James DeVoe, Inorganic Analytical Research Division, National Institute of Standards and Technology (NIST), Gaithersburg, MD for their careful review.

EXECUTIVE SUMMARY

The determination of lead in paint, dust, soil and other matrices is receiving increased attention because of the adverse health effects associated with exposure to low levels of this environmental contaminant. Because exposure to lead hazards may be minimized or prevented by appropriate detection, abatement or containment, the accurate and precise identification of lead levels in paint, dust and soil is an important environmental concern. The concentration of lead in paint, dust and soil samples may be determined either in the laboratory or in the field. In order for concentration data to be reliable, it is important to also calibrate instruments and benchmark analytical performance with the use of reference materials. These materials are homogeneous, well-characterized, and have a known concentration of the analyte(s) of interest. However, the availability of reference materials for the routine analysis of environmental lead samples is limited, and there are no standard protocols for the production of these materials.

This study was carried out to prepare a series of lead-containing paint and dust reference materials according to criteria established at a Lead Reference Materials Workshop sponsored by the U.S. Environmental Protection Agency. The criteria for the production of the materials, called Method Evaluation Materials (MEMs) included the following;

- lead concentration,
- material homogeneity, and
- characteristics of the matrix.

After the materials were prepared, the protocol for the preparation was validated by analysis of the materials for the following:

- measured lead concentrations within 20% of the target concentrations, and

- sample to sample variations (homogeneity) of the materials statistically non-significant relative to overall standard deviations.

The analyses were carried out by:

- the Research Triangle Institute, and
- 33 external laboratories.

Because a sufficient number of laboratories analyzed the MEMs using different selected extraction/analytical methods, statistical analysis of the data also allowed a comparison of laboratory performance using these proven methods.

Four MEMs were prepared at the following targeted lead concentrations:

- 100 μg/g in dust,
- 1500 μg/g in paint,
- 4000 μg/g in dust, and
- 40000 μg/g in paint,

from "real-world" lead-containing paint and dust, collected from households in North Carolina and California, abatement sites in Pennsylvania and a vacant hospital in Ohio.

The paint materials were collected as chips scraped from walls, woodwork and other surfaces. Aliquots were taken from each bag of chips, ground by hand using a mortar and pestle, and then analyzed to obtain estimates of the lead levels. Analysis was performed using microwave/acid extraction and measuring the lead levels by inductively coupled plasma emission spectrometry. Specific paint materials were chosen on the basis of these results to meet target concentrations. The paint materials chosen were then mechanically ground to a fine powder ($\leq$ 120 microns) and each batch prepared mixed thoroughly.

The dust was collected in home vacuum cleaners and also high efficiency particulate collection vacuum cleaners. The dust was sent to a commercial firm

for sterilization and then sieved to a particle size ≤250 microns. The sieved dust samples were each thoroughly mixed and were then subjected to preliminary analysis as described for paint, and batches selected relative to the target concentrations.

Prior to a round robin analysis of the selected, prepared materials verification analyses were performed.

The concentrations of the MEMs, determined by RTI to be acceptable relative to the target concentrations, were the following:

- 84.2 ± 11.9 μg/g - low lead-containing dust,
- 1410 ± 44.5 μg/g - low lead-containing paint,
- 4670 ± 330 μg/g - high lead-containing dust,
- 37900 ± 500 μg/g - high lead-containing paint, and

These samples were submitted in duplicate to laboratories for round-robin analysis.

The sample set submitted to round-robin analysis also included Standard Reference Materials (SRMs) of paint and "dust" (a soil SRM was used as a surrogate for dust) prepared and certified by the National Institute of Standards and Technology (NIST). The following Standard Reference Materials were included as single blind samples:

- 1162 ± 31 μg/g - NIST SRM 2711, Montana Soil, used as a surrogate dust sample
- 118700 ± 400 μg/g - NIST SRM 1579, Powdered Lead-based Paint.

The complete sample set included 2 bottles of each paint MEM, 2 bottles of each dust MEM, one bottle of paint SRM, and one bottle of "dust" SRM for a total of 10 bottles of samples. Each laboratory was asked to analyze two aliquots of

each sample for a total of 20 analyses. Laboratories were recruited for participation in the round robin on the basis of their experience and willingness to carry out the analyses by methods commonly used to analyze environmental lead samples:

- hotplate (HP) or microwave (MW) extraction followed by analysis by atomic absorption spectrometry (AAS) or inductively coupled plasma emission spectrometry (ICP) , and/or
- energy dispersive laboratory X-ray fluorescence (Lab XRF).

A total of 33 laboratories performed 42 different sets of analyses, as follows:

Methodology	Number of Performances
• MW/AAS	7
• HP/AAS	9
• MW/ICP	9
• HP/ICP	10
• Laboratory XRF	7

The number of laboratories analyzing by each method (a minimum of seven (7) performances were required) was sufficient for a statistical comparison of methods. Results of the statistical analysis provided data for determination of the method mean, consensus value, repeatability and reproducibility of methods for each test sample. The method means and consensus values indicated that the protocol produced samples having acceptable concentrations relative to the target concentrations. Precision data indicated that the average sampling coefficient of variance (cv) was 1.37%; the 95% upper confidence limit of the cv was 2.5%; and therefore, 95% of all test samples were found to have a concentration within 5% of the consensus value (95% to 105 % of the consensus value). Therefore, the homogeneity of the materials was considered to be acceptable.

A comparison of data by method showed that the MW/AAS method gave results with the highest concentrations for all six test samples. Laboratory XRF gave the lowest results for 5 out of 6 test samples. A pairwise comparison of method means indicated that these two methods also showed the most statistically significant differences. When the data for matrices was pooled, the repeatability (within-lab variation) of the laboratory XRF method was shown to be best (4.8%) for all methods tested (range of methods: 4.8% - 12.9%); but the reproducibility (between-lab variation) of this method (19.4%) was poor (range of methods: 11.7% - 21.0%). The reproducibility of the MW/ICP method was the best (11.7%) across all concentrations of the test samples.

The poor reproducibility of the Lab XRF method was attributed to:

- failure to request that laboratories follow the same protocol for the analyses, and/or
- the provision of an inadequate number of calibration standards for the instrumental analysis. (This is suggested by the quadratic appearance of log recovery plots for the Lab XRF method.)

Results also indicated that recoveries for analyses by AAS showed a positive bias relative to ICP results. This bias was believed to result from the lack of background correction by a number of laboratories analyzing by AAS. It is also possible that the concentrations were suppressed in the ICP measurements, but laboratories analyzing by ICP were warned about signal suppression arising from matrix effects, and were instructed to dilute solutions for analysis into a 1 - 10 μg/mL range to minimize these effects. It is suggested that further studies be performed to investigate the bias observed in results reported by the analytical methods, and the poor reproducibility shown by Laboratory XRF.

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INTRODUCTION

1.1 OVERVIEW

As a result of the growing concern about the adverse health effects associated with exposure to lead in the environment, the identification and assessment of hazards from lead-based paint (LBP) and LBP-containing dust and soil have become critical environmental issues. Because the identification of LBP hazards requires either field or laboratory analysis, an increasing number of lead-containing matrices are being submitted to analysis. Unfortunately, there is a lack of reference materials, materials of known concentrations, to support the reliability of the results. Regulations in support of the establishment of lead tester certification programs (Title X[1]) and a National Lead Laboratory Accreditation Program[2] (NLLAP) have been promulgated to ensure that these decisions are based upon analytical data that is accurate, reproducible and representative.

The analysis of reference materials, well-characterized, homogeneous materials of known concentration, is necessary for the accurate calibration of instruments and essential to the evaluation of laboratory performance in the preparation and analysis of samples. Two types of reference materials are important in analytical chemistry quality assurance:

- standard reference materials (SRMs) produced and certified by the National Institute of Standards and Technology, and
- performance evaluation materials (PEMs).

Of the two types of reference materials, SRMs are more homogeneous and more stringently characterized. The analytical uncertainty for SRMs is less than or equal to 10 percent, as compared to 10 - 25 percent for PEMs[3]. Thus, SRMs are more costly and less available for routine quality assurance/quality control (QA/QC) activities. PEMs are more easily prepared, less costly than SRMs, and

are therefore better suited for routine QC checks.

The purpose of this study was to develop and test a protocol for the production of homogeneous performance evaluation materials, hereafter called Method Evaluation Materials (MEMs), as prescribed by the U. S. Environmental Protection Agency (U.S. EPA)-sponsored Lead Reference Materials Workshop[4] (LRMW) held in May, 1991. The protocol was tested by round-robin analysis of the concentration and homogeneity of the MEMs produced following the protocol. In addition to the provision of concentration and homogeneity data for the series of MEMs, the results of the round-robin allowed a comparison to be made of proven extraction/analytical methods used by the participating laboratories.

The preparation and verification of the protocol was designed relative to the following:

- establishment of target concentrations and homogeneity for the method evaluation materials, consistent with proposals at the Lead Reference Materials Workshop,[4]
- collection of real-world paint and dust,
- preparation of materials at the targeted concentrations,
- verification of the concentration and homogeneity of the MEMs by analyses at RTI,
- designation of methods for analysis in the round-robin,
- recruitment of laboratories for measurement by select extraction/analysis methods,
- statistical design of the round-robin
  - identification of replicates,
  - identification of Standard Reference Materials to be submitted as blinds, and
  - identification of a minimum number of laboratories analyzing by a particular extraction/analysis,
- round-robin analysis of MEMs and SRMs,

- statistical analysis of results, and
- conclusions and recommendations for further study.

The results of the round-robin study were expected to provide the following data:

- method mean - a concentration for a test sample determined from averaging the results reported by a specified method of analysis,
- consensus value - a concentration for a test sample determined by averaging the method means determined by different laboratories and/or methods,
- recovery by method - a ratio of the method mean to the consensus value, expressed as percentage,
- repeatability - within-lab variation, the relative standard deviation (%) determined for replicate samples analyzed in one laboratory,
- reproducibility - between-lab variation, the relative standard deviation (%) determined for replicate samples analyzed by laboratories using the same method, and
- sample-to-sample variation - the homogeneity of the material determined from a test of the hypothesis that the variation between replicate aliquots is zero.

The interpretation of data was applied to examine the following:

- protocol for MEM preparation by comparing the consensus values with the targeted concentrations, with the expectation that the targeted concentrations and consensus values agreed within 20%;
- sample-to-sample variation by comparing repeatability and reproducibility of replicate samples analyzed by the same method; and
- comparison of methods by determining
  - the 95% confidence interval of method means, and
  - the statistically significant differences by pairwise comparison of method means.

1.2 REPORT

This report describes the preparation of paint and dust method evaluation materials and verification of the preparation protocol. The reader may refer to the following sections for specific information:

- design and preparation of the materials - Sections 2 and 3,
- round-robin analysis - Section 4,
- statistical analysis of results of the round-robin - Section 5.
- summary and conclusions - Section 6, and
- suggestions for further study - Section 7.

SECTION 2.0
DESIGN OF THE METHOD EVALUATION MATERIALS

2.1 CRITERIA ESTABLISHED BY THE LEAD REFERENCE MATERIALS WORKSHOP

The design for MEMs was developed in a reference materials workshop held May 13-14, 1991 in Washington, DC.[4] The nature of "real-world" samples, health effects, and regulations were considered to be the principal driving forces for the preparation of MEMs. Subsequently it was decided that the matrices of the reference materials match the matrices of the samples typically submitted to the laboratory for analysis. Matrix-matching is critical because the nature of the matrix is a significant factor in the effectiveness of extracting lead from paint and dust samples; i.e., old dried paint samples extract differently from newly-prepared paint films.[5] Matching the matrix of reference materials and samples, i.e., binders, particle size, is also important for accurate analysis by Laboratory XRF.

2.1.1 Paint

It was decided in the workshop that paint be collected from dwellings at least 40 years old. Assuming an aliquot of 0.25 g for atomic spectroscopic analysis, it was proposed that the material be ground to a particle size of ≤200 microns in order for the aliquot to be representative of the bulk sample. A concentration range of 500 to 50,000 μg/g (0.05% to 5%) was proposed to cover the current regulations.

2.1.2 Dust

It was suggested in the Workshop that "real-world" dust be collected for preparation of reference material. No decisions were made about particle size, although it was decided that an appropriate concentration range for reference materials for lead in bulk dust of 50 to 10,000 μg/g be established to encompass a concentration range inclusive of lead in hand wipes to post-abatement lead levels.[4]

2.2 CONCENTRATIONS PROPOSED FOR METHOD EVALUATION MATERIALS

It was decided that, practically, only a limited number of MEMs could be analyzed as a means of evaluating the preparation protocol. Therefore, in order to verify the preparation protocol by a determination of concentration and homogeneity, it was decided that paint and dust MEMs be prepared only at two different concentrations, and that each of the two concentrations be split into two replicates and bottled as two separate samples. This would provide a total of four samples of paint, and four samples of dust for testing.

For dust samples, a low level sample (approximating household dust) and a high level sample (approximating post-abatement dust), were proposed. For paint samples, a low level paint sample (having a concentration between the Consumer Product Safety Commission (CPSC) action limit[6] of 600 μg/g and the Department of Housing and Urban development (HUD) action level[7] of 5000 μg/g), and a high level sample (approximating a concentration commonly detected on the exterior of older dwellings) were targeted. The following concentrations were proposed for the MEMs:

- 100 μg/g - low level dust (household),
- 1500 μg/g - low level paint,
- 4000 μg/g - high level dust (post-abatement), and
- 40000 μg/g - high level paint (exterior).

SECTION 3.0
PREPARATION OF THE METHOD EVALUATION MATERIALS

As noted, an important consideration for the preparation of reference materials is matching the matrix of the reference material to the matrix of the samples typically submitted to analysis. Therefore, the preparation of the method evaluation materials used in this study required the collection of "real-world" paint and dust samples.

3.1 PAINT

Paint samples submitted to laboratory analysis are often multiple layers of different kinds of paint that have embrittled from age and weathering. In order to emulate samples submitted to a laboratory, the method evaluation materials in this study were prepared from "real-world," multi-layered paint.

3.1.1 Collection of Materials

The collection of real-world samples was facilitated by contacts acquired through RTI tasks in support of EPA programs for lead-based paint and lead-based paint-containing matrices. The tasks performed for the EPA included coordination of a preliminary round-robin[8] for the evaluation of spectroscopic methods for the analysis of lead in paint, dust and soil; coordination of Lead Reference Materials Workshop[4]; and collection of lead-based paint for standard reference materials (SRMs) prepared by the National Institute of Standards and Technology (NIST). As a result of these tasks, RTI established an extensive repository of lead-based paint containing matrices. This repository contains paints from interior walls, interior woodwork, and exterior trim collected from abatement and demolition projects across the country. The specific paint materials used to prepare the test MEMs for this study were collected from a vacant hospital in Athens, Ohio. The paint collected from this site was old, and multi-layered from regular repaintings since the establishment of the hospital in

the late 19th century. It was peeling from the substrate to such an extent that the firm of Osborne and Assoc.,[9] an abatement contractor, was able to collect the chips by sweeping the floors and cold-scraping the walls and woodwork with squeeges.

3.1.2 Selection of Bulk Materials

Preliminary screening analyses of paint samples were carried out at the time of sample custody. Aliquots of several grams each were removed from each of the bulk samples and ground by hand with a mortar and pestle. Aliquots were then removed from the ground material and extracted by a microwave (MW) method[10] utilizing a combination of nitric acid (HNO_3) and hydrochloric acid (HCl). The concentration of lead in the extracts was measured by inductively coupled plasma emission spectrometry (ICP).

The majority of the samples collected at the Athens site contained lead at concentrations in the range of 5% to 40%, but two bulk paint samples having concentrations of 3.8% and 0.36% were also identified. The 3.8% and 0.36% materials were chosen for the preparation of the MEMs; though well above the target of 0.15%, the 0.36% material was the lowest level available in the repository.

3.1.3 Grinding

Both bulk paint samples were ground to a particle size of ≤250 microns (μm) in a crossbeater mill[11], and then ground to a particle size ≤120 μm in a Retsch[12] grinder.

3.1.4 Blending

The ground paints were individually mixed for 30 minutes in a Turbula[13] blender.

3.1.5 Determining the Effect of Aliquot Weight on Analytical Results

One of the concerns in development of a reference material is the effect of aliquot weight on the analytical results. It is desirable to maximize an aliquot size in order to minimize errors associated with lack of homogeneity in the sample, while still achieving acceptable analyte recovery, i.e.,) 90%. Maximizing aliquot size is particularly important for samples having lead concentrations near the detection limit of the analytical method used. Therefore, the effect of the aliquot weight on the analytical results was investigated by removing aliquots from the high-lead and low-lead paint bulk materials, and analyzing the aliquots by the MW/ICP method[10].

Aliquot sizes of 50 mg, 100 mg, and 250 mg were selected for investigation because these aliquot weights are commonly used in the analysis of environmental samples with lead concentrations in a normal to high range (>10 μg/g to 120,000 μg/g). For the determination, samples at the three different aliquot weights were removed in duplicate from each bulk material. For example, two 50 mg aliquots, two 100 mg aliquots, and two 250 mg aliquots were removed from the prepared low and high lead-containing paint materials, yielding a total of 12 samples for analysis. The results of the analyses are given in Table 1. A statistical evaluation showed all of the measured concentrations to be equivalent at the 95% confidence interval, except for the 250 mg aliquot of low paint. A review of the analytical data indicated that this sample was measured at an instrumental (ICP) concentration of 41.5 μg/mL, well above the measured concentrations of the other paint samples (and an instrumental range concentration later prescribed for the round-robin evaluation of these materials). Because of the high instrumental concentration of the 250 mg aliquot, ICP signal suppression was considered a source of the depressed concentration of this sample relative to the 50 and 100 mg aliquots. (The difference in AAS and ICP results will be discussed in Section 5.) An aliquot weight of 100 mg was selected for the paint materials because this

Table 1. Concentrations of Lead Measured in Paint and Dust Method Evaluation Materials Relative to Changes in the Aliquot Weight for Extraction

Sample	Mean (µg/g) ± SD (% RSD) (n=2)		
	Aliquot Size		
	50 mg	100 mg	250 mg
Low Paint	3600 ± 7.06 (0.196)	3530 ± 42.4 (1.20)	3310 ± 28.3 (0.854)
High Paint	36800 ± 1203 (3.27)	36200 ± 283 (0.781)	36000 ± 425 (1.18)
Low Dust	97.4 ± 29.2 (29.9)	79.8 ± 0.42 (0.53)	81.2 ± 0.71 (0.87)
High Dust	4340 ± 503 (11.6)	4160 ± 84.9 (2.04)	4100 ± 6.97 (0.17)

Legend:

% RSD = Percent Relative Standard Deviation

weight gave consistently high recoveries. Increasing the weight to 250 mg would not improve precision.

3.1.6 Production of Target 0.15% Material

As stated earlier, a bulk paint material having a lead concentration of about 1500 $\mu g/g$ (0.15%) could not be located. Achieving this target concentration was considered important to the evaluation process, and therefore, when a source of bulk paint having a lead concentration lower than 0.36% could not be found, an attempt was made to determine if separation of the layers of the multi-layered chips would yield layers containing lead at different concentrations. It was believed that the most recently applied layers, i.e., the outermost layers, would contain lead at the lowest levels.

The 0.36% paint material was found to be a combination of multi-colored layers of paint; therefore, it was possible to identify and separate (by hand) chips that appeared to have the same colored layers, and were believed to have an identical painting history. From these selected chips, the outermost layers were removed with a scalpel to yield a paint sample representing the most recent painting. This method was used to isolate a material that, upon analysis, showed a concentration of 0.15%. The 0.15% material was carried through all the preparation steps (grinding, blending) described for the preparation of the 0.36% material. The previously prepared 3.8% material, and the 0.15% material were designated as "high paint" and "low paint," respectively.

3.1.7 Preliminary Verification of Concentration and Homogeneity

The concentrations of both the low and high paint materials were determined by analyzing 100 mg replicate aliquots (except the low paint material, where n =1) of the prepared materials by the MW/ICP method.[10] Results of the concentration verification, given in Table 2, indicated that the targeted concentrations for the selected samples were achieved. Acceptable homogeneity was achieved as indicated by a relative standard deviation (RSD) of 1.87% for the

Table 2. The Concentration and Homogeneity (RSD)
of Paint and Dust Method Evaluation Materials
Determined at RTI by Microwave Extraction
with Measurement by Inductively Coupled Plasma Emission Spectrometry

	Concentration (μg/g) $\pm$ SD	RSD (%)
High Paint	36300 ± 679 (n=6)	1.87
Low Paint	1400 (n=1)	---
High Dust	4130 ± 61.8 (n=4)	1.50
Low Dust	80.5 $\pm$ 0.938 (n=4)	1.17

high paint. Only one sample was analyzed for the preliminary verification of concentration of the low paint; therefore, precision data were not available.

3.2 DUST

3.2.1 Collection of Materials

The RTI repository of lead-contaminated dust materials includes household, hotel, street, and post-abatement dust. Household and hotel dust samples were collected as vacuum cleaner bags; post-abatement dust was supplied to RTI as High Efficiency Particulate Air (HEPA) vacuum cleaner bags from abatement sites in the Midwestern and Eastern United States. Street dust was collected from street sweepers in Durham, North Carolina.

Household dust, collected from local households and from households in California, was used to prepare the low dust MEM for this evaluation. The high dust MEM was prepared from HEPA-vacuumed dust collected from abatement sites in Pennsylvania.

3.2.2 Sterilization

Because dust samples contain large amounts of debris, animal protein and microbiological organisms, all bulk dust samples were sterilized by irradiation prior to handling. Upon receipt at RTI, the bulk dust was shipped to Neutron Products, Inc.,[14] and gamma-irradiated for 12 hours for a total minimum dose of 2.5 MRads.

Although the samples were only visually examined for the growth of microbiological organisms, it did not appear that the dust samples were recontaminated from the post-sterilization opening of containers or from atmospheric moisture. The bulk dust appeared to be stable after sterilization.

3.2.3 Removal of Debris

The sterilized bags of dust were returned to RTI and individually sieved to remove debris and hair. The dust was sieved through a coarse (2.00 mm) and fine

(250 μm) screen using a Ro-Tap[15] apparatus.

3.2.4 Selection of Bulk Materials

Aliquots of 100 mg were removed from individual bags of sieved dust and analyzed by the MW/ICP method[10] in order to identify materials with appropriate lead concentrations for the preparation of the MEMs.

3.2.5 Blending

Because the weight of sieved dust from one vacuum cleaner bag was insufficient to provide enough material for the low dust sample, batches of sieved household dust with concentrations approximately equal to 100 μg/g were blended for 30 minutes in a Turbula[13] blender to achieve an adequate weight of dust at the targeted concentration. The concentration of lead in the blended material was determined by removing four 100 mg aliquots and analyzing each by the MW/ICP method.[10] The results of the analysis for the blended household dust indicated a concentration of 80 μg/g, as targeted for the low dust sample.

It was not necessary to blend bulk samples of post-abatement dust because the weight of the sieved sample was sufficient for the round-robin test samples. The concentration of the post-abatement dust was found to be 4100 μg/g, as targeted for the high dust sample.

3.2.6 Determining the Effect of Aliquot Weight on Analytical Results

The effect of aliquot weight on analytical results was also investigated for the prepared dust samples. Aliquots of 50 mg, 100 mg, and 250 mg were removed in duplicate from each of the low and high dust samples. The aliquotting was analogous to that carried out for the paint materials; a total of 12 aliquots were removed for analysis by the MW/ICP method[10]. Results of the analyses, given in Table 1, indicated that the measured concentrations were consistent over the 50 t(100 mg range of aliquot weights. Improvements in precision were observed with increases in aliquot weight. An aliquot size of 100 mg was prescribed for the

analyses because this weight gave acceptably precise results, and was consistent with the aliquot size prescribed for the analysis of paint samples. The 95% confidence intervals for the concentrations of the 50, 100, and 250 mg aliquots were equivalent.

3.2.7 Preliminary Verification of Concentration and Homogeneity

The concentrations of the high and low dust samples were determined by taking replicate 100 mg aliquots of the prepared materials and analyzing by the MW/ICP method.[7] The results of the analyses are given in Table 2. Acceptable target concentrations and homogeneity (RSD ≤ 1.50%) were achieved.

3.3 BOTTLING THE TEST SAMPLES

The method evaluation materials and the standard reference materials were bottled by direct weighing of prepared materials into screw-cap bottles. Approximately 150 bottles of each matrix were prepared by accurately weighing 5 grams each of the high and low paint, and 2 grams each of the high and low dust into 20 mL plastic screw-cap bottles. During the transfers, the four stock containers of the bulk high and low paint and dust materials were tumbled in all directions several times after the removal of every 5 to 7 samples. The bottles containing the MEMs were numbered sequentially to track the loading from the bulk material. The sequence number was recorded by RTI.

The NIST Standard Reference Materials were bottled using the same procedure as the method evaluation materials, i.e., 5 grams of NIST SRM 1579, and 2 grams of NIST SRM 2711 were weighed into 20 mL plastic screw cap bottles. The bottles of bulk SRMs were also tumbled through all directions after every 5 to 7 aliquots were taken, and SRM samples were sequentially numbered to track the loading from the stock material into the 20 mL bottles. The sequence number was recorded by RTI.

3.4 FINAL VERIFICATION OF CONCENTRATION OF THE METHOD EVALUATION MATERIALS

Five bottles were removed at random from each of the four prepared sets of method evaluation materials (high paint, low paint, high dust, and low dust). From each bottle, five 100 mg aliquots were removed. (Bottles were tumbled through all axes between the removal of each aliquot.) The aliquots were analyzed by the MW/ICP method[10]. The final concentrations of the bottled materials yielded samples with concentrations within 20 percent of the targeted range (100 μg/g - 100,000 μg/g):

- 84.2 ± 11.9 μg/g - low dust,
- 1060 ± 21.2 μg/g - NIST SRM 2711
  (1162 ± 31 μg/g - certified value),
- 1410 ± 44.5 μg/g - low paint,
- 4670 ± 330 μg/g - high dust,
- 37900 ± 500 μg/g - high paint, and
- 116000 ± 3500 μg/g - NIST SRM 1579
  (118700 ± 400 μg/g - certified value).

The targeted concentrations for the paint and dust samples, the sources of the samples, and the final verified concentrations are presented in Table 3.

Table 3. Test Sample Set for Round-Robin Analysis. Source of Bulk Materials, Targeted Concentration and Final Concentration of Bottled Materials Determined at RTI by Microwave Extraction with Measurement by Inductively Coupled Plasma Emission Spectrometry

Samples	Source	Targeted Concentration (μg/g)	Concentration (MW/ICP) Mean (μg/g) ± SD(%RSD) n=25
Low Paint (P-1, P-4)	Athens, Ohio	1500	1,410 ± 44.5 (3.16)
High Paint (P-3, P-5)	Athens, Ohio	40,000	37,900 ± 500 (1.35)
Paint SRM (P-2)	NIST SRM 1579	120,000	118,700 $\pm$ 400 (0.34) (certified value)
Low Dust (D-2, D-4)	Household dust, NC & CA	100	84.2 ± 11.9 (14.1)
High Dust (D-1, D-5)	Post-abatement dust, PA	4000	4,670 ± 330 (7.07)
Dust SRM (D-3)	NIST SRM 2711	1000	1162 $\pm$ 31 (2.67) (certified value)

Legend:

MW = Microwave Digestion Method
ICP = Inductively Coupled Plasma Emission Spectrometery

SECTION 4.0

ROUND-ROBIN ANALYSIS OF THE METHOD EVALUATION MATERIALS

Following preparation of the MEM materials and their analysis within RTI, the materials were further evaluated by round-robin analysis. A statistical design for the round robin was developed by the U.S. EPA and is presented in Appendix A-1.

4.1 ROUND-ROBIN DESIGN

The design called for each laboratory to receive as blind samples two bottles of each of the four MEMs. Each laboratory was also to receive a sample of each matrix at a third concentration. This third material, a standard reference material (SRM), provided one additional sample per matrix, and was also submitted as a blind sample. A suggestion was made to include two blind samples of the same SRM, consistent with the submission of two MEM samples of the same concentration, but this suggestion was rejected because of the increased number of analyses, and thus cost incurred, for the participating laboratories. As a result, a total of ten samples were planned for submission to round-robin analysis.

Each laboratory was requested to remove two aliquots from each sample, thereby preparing and analyzing each sample in duplicate. As a result, a total of twenty (20) results were to be reported for each laboratory operation.

The samples were to be either extracted using a specified hotplate or microwave method, and analyzed by atomic absorption spectrometry (AAS) inductively coupled plasma emission spectrometry (ICP); or to be analyzed by Laboratory X-ray Fluorescence (Lab XRF). These methods were chosen because of their relevance to analyses carried out for environmental lead samples. Laboratory XRF was included because it had performed successfully using the protocols outlined in the EPA Urban Soil Lead Abatement Demonstration Project (Three City Study)[16]. The methods of analysis (extraction/analytical and

Laboratory XRF) resulted in a total of five candidate methods:

- Method 1 - MW/AAS,
- Method 2 - HP/AAS,
- Method 3 - MW/ICP,
- Method 4 - HP/ICP, and
- Method 5 - Laboratory XRF.

ISO Guide 35[17] (Appendix A-2) provided a reference for the statistical evaluation, and for expressing the results of the homogeneity testing. (See Section 5.6.)

4.2 RECRUITMENT OF LABORATORIES

A number of laboratories were recruited on the basis of their participation in a previous round robin[8], or as contacts facilitated through other tasks carried out by the Research Triangle Institute (RTI) in support of EPA lead programs. The goal was the recruitment of a minimum of eight to ten laboratories for analysis of the samples by each of the five operations. A total of 36 laboratories were recruited for participation in the round-robin; 11 of the 36 laboratories agreed to analyze samples by two methods, resulting in the potential of 47 analytical operations. Projected participation by operation was a follows:

- MW/AAS - 9 operations
- HP/AAS - 9 operations
- MW/ICP - 9 operations
- HP/ICP - 12 operations
- Laboratory XRF - 8 operations

At the completion of the round, results for 42 operations were reported by 33

laboratories. A list of participating laboratories is provided in Appendix B.

4.3 ROUND-ROBIN ANALYSIS

4.3.1 Standard Operating Procedures

Standard Operating Procedures (SOPs) were sent to all participating laboratories prior to the submission of the test samples. The protocols provided to laboratories are given in Appendix C.

4.3.1.1 Analysis by Atomic Absorption Spectrometry or Inductively Coupled Plasma Emission Spectrometry --

The EPA/AREAL report, "Standard Operating Procedures for Lead in Paint by Hotplate- or Microwave-based Acid Digestion and Atomic Absorption or Inductively Coupled Plasma Emission Spectrometry,"[10] was sent to laboratories analyzing by AAS or ICP. Laboratories analyzing by these methods were instructed to follow the protocols provided in the SOP. The SOP is provided in Appendix C-1.

4.3.1.2 Analysis by Laboratory X-ray Fluorescence

A reference draft protocol from the US EPA Environmental Monitoring Systems Laboratory (EMSL)/Las Vegas, "Standard Operating Procedures for Energy-Dispersive X-ray Fluorescence Analysis of Lead in Urban Soil and Dust Audit Samples,"[18] was provided to laboratories analyzing by laboratory X-ray fluorescence. Laboratories were asked to follow the protocol specified in the EMSL/Las Vegas document only if the laboratory did not have a protocol for the analysis of dust. The draft SOP is included in Appendix C-2 to provide a record of the information sent to participating XRF laboratories.

Two dust audit samples prepared by the EMSL/Las Vegas for the EPA Urban Soil Lead Abatement Demonstration Project[16] were provided to the laboratories analyzing by Laboratory X-ray fluorescence. These audit materials, BAL-1 and CIN-1, had lead concentrations of 58 μg/g and 2275 μg/g, respectively.

The audit samples were provided to all laboratories because some of the participating laboratories did not have suitable calibration standards for the analysis of dust. In order to establish a consistency in the instrument calibration, all laboratories using the XRF method were asked to use BAL-1 and CIN-1 to set up a calibration curve for the analysis of the dust samples.

4.3.2 Letter of Instructions

A letter of instructions was submitted to the laboratories along with the set of test samples. Exemplary letters sent to AAS/ICP and Laboratory XRF participants are provided in Appendix D.

Laboratories were requested to tumble every sample bottle prior to analysis, and to carry out analyses in duplicate. If an extraction technique was used, the laboratory was asked to remove two 100 mg aliquots, carry each aliquot through the extraction procedure, and analyze the extract. XRF laboratories were instructed to remove two sufficiently large aliquots to prepare "infinitely thick" samples for analysis.

4.3.3 Data Reporting Form

Laboratories were requested to report results to RTI in a Data Reporting Form provided by RTI. The form indicated the name of the laboratory and its assigned identification number for the round-robin, as well as the extraction and/or analytical method to be performed for the analyses. A space was available for the laboratory to indicate its experience (number of years) with the method. Exemplary Data Reporting Forms are provided in Appendices D-1 and D-2, for the extraction methods and Laboratory X-ray fluorescence, respectively. Sequence numbers for loading samples shipped to a participating laboratory were recorded on an RTI copy of the laboratory's Data Reporting Form. Exemplary copies are provided in Appendix D-3. Completed Data Reporting Forms (coded by laboratory, and categorized by method) are provided in Appendices E-1 through E-5.

4.3.4 Instrument Parameter Forms

Forms were included with the set of samples for the laboratories to provide instrumental parameters appropriate to the analyses. AAS/ICP laboratories were asked to provide information including manufacturer, model number, background correction, and calibration data. Laboratory XRF parameters, i.e., manufacturer, sample preparation, X-ray source, were requested of these laboratories. Laboratories were requested to submit the forms to RTI along with the Data Reporting Forms. Instrumental parameter forms are provided in Appendices D-1 and D-2 for AAS/ICP and Laboratory XRF analyses, respectively. Results were due to RTI no later than April 30, 1992.

4.3.5 Responses From Participating Laboratories

A total of 42 sets of results were reported to RTI from 33 participating laboratories. (Nine laboratories analyzed the test samples by two different methods.) The final distribution of results by method was as follows:

- MW/AAS - 7,
- HP/AAS - 9,
- MW/ICP - 9,
- HP/ICP - 10, and
- Laboratory XRF - 7.

Two laboratories did not return MW/AAS data because the laboratories encountered problems with melted and/or imploded plastic centrifuge tubes. (The tubes were required for the microwave extraction procedure,[10] and were supplied by RTI. One laboratory carried out subsequent analyses using a total digestion by a HP/ICP method; the results from the total digestion were not included in the statistical analysis. Two laboratories encountered problems believed to be attributed to the homogeneity and/or prescribed aliquot size for the low dust

material. One laboratory found that repeated analyses of the same extract of the low dust sample gave repeatable results, yet poor repeatability was achieved when replicate aliquots were removed, and each was extracted and analyzed.

4.3.6 Notification Of Results

Following the statistical analysis of results (presented in Section 5), letters were sent to participating laboratories summarizing the results of the preliminary statistical analysis. The letter included tables from a draft paper to be published in the proceedings of the American Chemical Society Symposium, "Lead Poisoning in Children: Exposure, Abatement and Program Issues,"[19] held in August, 1992. This letter is provided in Appendix F.

SECTION 5.0
STATISTICAL ANALYSIS OF RESULTS

A statistical analysis[20-22] of the data submitted by the participating laboratories was performed to determine the following:

- mean concentration by method for each of the six test samples,
- consensus value for each of the six test samples,
- statistically significant differences between method means, determined for each of the six test samples,
- homogeneity (sample-to-sample variation of the material),
- repeatability (within-lab variance) by method, and
- reproducibility (between-laboratory variance) by method.

The report of the statistical analysis by RTI statistician Dr. Larry Myers is provided in Appendix G-1. The statistical analysis was reviewed by EPA statistician Mr. Jack Suggs. This review is provided in Appendix G-2.

5.1 CENSORED, MISSING DATA

A total of 33 laboratories reported results for 42 combinations of extraction/analysis methods. Analyses of 10 test samples (blind duplicate high and low paint and dust samples, and single blind samples of SRMs 1579 and 2711) were carried out in duplicate for a total of 20 reported results per extraction/analysis. One laboratory reported triplicate results; two results were not reported. Therefore, a total of 848 results were examined statistically. The original data entries for statistical analysis (raw data) is provided in Appendix G-3; missing and censored observations are provided in Appendix G-4.

5.2 OUTLYING DATA

At the outset, results that were reported non-quantitatively, i.e., less than a specific concentration (primarily for the low dust sample), were excluded from the statistical analysis, yielding 820 results to be examined for outliers.

For each of the six combinations of matrix (dust, paint) and level (high, low, and SRM), a nominal concentration was calculated as the median of all reported results from the extraction methods. Laboratory XRF data were excluded because of the following factors:

- a preliminary statistical examination of the data indicated a negative bias relative to data for the extraction methods, and
- XRF analyses were not carried out using a standardized SOP, as in the case of the AAS/ICP analyses.

A recovery for each extraction method result was calculated as the ratio of the reported concentration divided by the nominal concentration. Using recoveries between 0.35 and 2.00, the average and standard deviation of the recovery was calculated for each of the method (5) by matrix (2) by level (3) combinations (a total of 30 combinations). (The restriction to recoveries between 0.35 and 2.00 was a prescreen intended to remove grosser outliers having the potential of distorting the final means and standard deviations.) For each of the 820 reported results, a score for the recovery was calculated by subtracting the average recovery from the individual calculated recovery and dividing by the standard deviation of recovery for the given combination. Any measurement whose absolute recovery score exceeded 2.76 was excluded as an outlier. (Candidate outlying observations are provided in Appendix G-5.) This corresponded to the upper and lower one-half of one percent of a normal distribution. As a result of this screening, an additional 28 reported results were excluded, allowing a total of 792 results for statistical analysis.

5.3 METHOD MEANS

The method mean for each of the six samples (low paint, high paint, paint SRM, low dust, high dust, and dust SRM) was determined as the average of all reported results, excluding censored results and outliers. Standard deviations and relative standard deviations (RSDs) were determined. RSDs were found to be in the ranges of 1.8% to 11.8% for the paint samples, and 2.2% to 9.2% for the dust samples. These results are presented in Tables 4 and 5, and in Appendix G-6.

5.4 CONSENSUS VALUES

Consensus values for each of the six samples were calculated as an average of the method means for the four extraction methods. The standard deviation of the consensus value for a given sample was determined as the pooled standard deviation of the mean by method. These values are provided in Tables 4 and 5, and in Appendix G-6. (The standard deviations calculated and provided to the laboratories in the notification letter differ from the standard deviations given in Tables 4 and 5 because the data reported to laboratories were based upon preliminary calculations of simple standard deviations of the means. After the notification letter was sent, it was decided that pooled standard deviations were more statistically appropriate. Pooled standard deviations for the consensus values were then determined and are given in Tables 4 and 5.)

For the reasons given for the exclusion of Laboratory XRF data from the determination of a recovery score, Laboratory XRF values were also excluded from determination of the consensus values. Method recoveries were calculated as a ratio of method means to the consensus values, and are presented as percentages in Table 6.

Table 4. Consensus Values and Method Means
for Paint Samples Submitted to Round-Robin Analysis

Matrix/ Sample No.	Consensus Value[a] (μg/g) ± SD[b] (%RSD)	Method	Method Mean (μg/g) ± SD (% RSD)
High Paint (P-3, P-5)	37,632 ± 861 (2.3)	MW/AAS	41,281 ± 1,274 (3.1)
		HP/AAS	36,921 ± 713 (1.9)
		MW/ICP	36,654 ± 672 (1.8)
		HP/ICP	35,670 ± 796 (2.2)
		Lab XRF	27,404 ± 1,567 (5.7)
Low Paint (P-1, P-4)	1690 ± 63 (3.8)	MW/AAS	1,896 ± 63 (3.3)
		HP/AAS	1,661 ± 74 (4.5)
		MW/ICP	1,603 ± 45 (2.8)
		HP/ICP	1,600 ± 66 (4.1)
		Lab XRF	1,034 ± 76 (7.4)
Paint SRM (P-2) NIST 1579 Certified Value: 118,700 ± 400	109,859 ± 6521 (6.0)	MW/AAS	122,432 ± 6,507 (5.3)
		HP/AAS	104,340 ± 8,681 (8.3)
		MW/ICP	118,281 ± 2,476 (2.1)
		HP/ICP	94,382 ± 7,021 (7.4)
		Lab XRF	112,721 ± 13,259 (11.8)

[a]Lab XRF excluded from consensus value determination.
[b]Pooled standard deviations

Legend:

MW = Microwave Method (EPA/AREAL)
HP = Hotplate Method (NIOSH 7082)
ICP = Inductively Coupled Plasma Emission Spectrometry
AAS = Atomic Absorption Spectrometry
XRF = X-Ray Fluorescence
SRM = Standard Reference Material

Table 5. Consensus Values and Method Means
for Dust Samples Submitted to Round-Robin Analysis

Matrix/ Sample No.	Consensus Value[a] (μg/g) ± SD[b]	Method	Method Mean (μg/g) ± SD (% RSD)
High Dust (D-1, D-5)	4550 ± 120 (2.7)	MW/AAS	4,847 ± 127 (2.6)
		HP/AAS	4,677 ± 103 (2.2)
		MW/ICP	4,281 ± 113 (2.6)
		HP/ICP	4,397 ± 133 (3.0)
		Lab XRF	2,485 ± 117 (4.7)
Low Dust (D-2, D-4)	104 ± 6 (5.8)	MW/AAS	114 ± 6 (5.3)
		HP/AAS	108 ± 7 (5.3)
		MW/ICP	98 ± 3 (3.1)
		HP/ICP	98 ± 9 (9.2)
		Lab XRF	93 ± 8 (8.6)
Dust SRM (D-2) NIST 2711 Certified Value: 1162 ± 31	1186 ± 44 (3.8)	MW/AAS	1,327 ± 72 (5.4)
		HP/AAS	1,173 ± 32 (2.7)
		MW/ICP	1,133 ± 24 (2.1)
		HP/ICP	1,112 ± 42 (3.8)
		Lab XRF	1,029 ± 33 (3.2)

[a]Lab XRF excluded from consensus value determination.
[b]Pooled standard deviation

Legend:

MW = Microwave Method (EPA/AREAL)
HP = Hotplate Method (NIOSH 7082)
ICP = Inductively Coupled Plasma Emission Spectrometry
AAS = Atomic Absorption Spectrometry
XRF = X-Ray Fluorescence
SRM = Standard Reference Material

Table 6. Recovery (%) by Method[a] (Relative to Consensus Values) of Paint and Dust Samples Submitted to Round-Robin Analysis

	Paint			Dust		
Method	High	Low	SRM	High	Low	SRM
MW/AAS	110	112	111	107	110	112
MW/ICP	97.4	94.9	108	94.1	94.2	95.5
HP/AAS	98.1	98.3	95.0	103	104	98.9
HP/ICP	94.8	94.7	85.9	96.6	94.2	93.8

[a]Lab XRF recoveries were not determined because these results were excluded from the determination of consensus values.

5.5 REPEATABILITY AND REPRODUCIBILITY

Repeatability and reproducibility are expressions of the within-laboratory and between-laboratory relative standard deviations measured for the six samples (low paint, high paint, SRM paint, low dust, high dust, and SRM dust), respectively. The values are based on the one-way analysis of variance of log recoveries, ignoring sample-to-sample differences (previously determined to be non-significant, and absorbed in the estimates of repeatability and reproducibility). Values determined for repeatability and reproducibility are provided in Table 7. The data in the table indicate that Laboratory XRF gave the most repeatable results, i.e., lowest percentage of variation for all six samples. The repeatability of Laboratory XRF is significant, subject to the caveat that the log transformation may not have sufficiently stabilized the variances in the methods. If the variances were stabilized by the log transformation, the reduction in within-lab variability observed for XRF measurements could be attributed to minimal steps required for sample preparation in XRF analysis.

Reproducibility is the more significant measure of variation in methods because it reflects both within-laboratory variance and between-laboratory variance. In general, the data in Table 7 indicate that Laboratory XRF is the least reproducible method for the analysis of the paint samples, whereas the MW/ICP method is the most reproducible method for the analysis of this matrix. The HP/ICP method showed the poorest reproducibility for the analysis of the low and high dust samples.

The differences in reproducibility of the Laboratory XRF method and the extraction methods were attributed to the instructions provided for the analyses. Laboratories using an extraction method were instructed to follow a specific protocol; whereas, XRF laboratories were provided with a protocol for dust

Table 7. Estimates of Sample-to-Sample Variation (Sample RSD), Repeatability (Within-Lab Variation), and Reproducibility (Between-Lab Variation) of Paint and Dust Samples Submitted to Round-Robin Analysis

		Methods				
Matrix	Parameter	MW/AAS	HP/AAS	MW/ICP	HP/ICP	Lab XRF
Low Paint	Mean (μg/g)	1896	1661	1603	1600	1034
	Sample RSD (%)	4.2	⟨ 0.1	⟨ 0.1	2.2	⟨ 0.1
	Repeatability (%)	11.5	12.4	11.9	9.7	3.4
	Reproducibility (%)	13.3	17.7	13.3	16.2	18.3
High Paint	Mean (μg/g)	41281	36921	36654	35670	27404
	Sample RSD (%)	⟨ 0.1	⟨ 0.1	⟨ 0.1	⟨ 0.1	⟨ 0.1
	Repeatability (%)	5.6	4.9	3.8	4.5	3.3
	Reproducibility (%)	9.5	7.1	6.5	8.2	15.7
Low Dust	Mean (μg/g)	114	108	98	98	93
	Sample RSD (%)	⟨ 0.1	⟨ 0.1	⟨ 0.1	8.9	⟨ 0.1
	Repeatability (%)	18.3	12.2	16.0	24.5	8.6
	Reproducibility (%)	20.2	20.6	16.5	35.3	22.2
High Dust	Mean (μg/g)	4847	4677	4281	4397	2485
	Sample RSD (%)	⟨ 0.1	3.5	⟨ 0.1	⟨ 0.1	⟨ 0.1
	Repeatability (%)	6.2	6.2	9.6	11.5	3.7
	Reproducibility (%)	8.9	8.9	10.6	13.7	13.2
Paint SRM	Mean (μg/g)	122432	104340	118281	94382	112721
	Repeatability (%)	7.2	6.2	4.4	12.5	1.3
	Reproducibility (%)	14.8	30.2	7.1	29.0	32.4
Dust SRM	Mean (μg/g)	1327	1173	1133	1112	1029
	Repeatability (%)	3.2	3.7	5.1	3.2	2.5
	Reproducibility (%)	14.2	8.9	7.5	12.7	8.7

Repeatability = Within-Lab Variation
Reproducibility = Between-Lab Variation

analysis only as a reference, and were instructed to follow their own protocol, if available.

The quadratic tendency observed in lab-specific recovery plots for analysis by Laboratory XRF suggested that calibrations were made with an inadequate number of standards. (Recovery plots are provided in Appendix G-7.) XRF laboratories provided their own paint standards for calibration, but two dust audit samples, BAL-1 and CIN-1, were provided by RTI for use as calibration standards for the analysis of dust. It is possible that instructions to generate a dust calibration curve using only the two audit samples, BAL-1 and CIN-1, resulted in the poor reproducibility observed for the dust samples. However, it should be noted that laboratories provided their own standards for the calibration of paint; and average reproducibility for this matrix was poorer than the average reproducibility for the analysis of the dust. On the basis of these results, it appears that the calibration differences, alone, do not explain the high value for reproducibility by Laboratory XRF.

In order to provide a graphical description of the differences in repeatability and reproducibility with concentration, the results of the analysis of variance (expressed in $\mu g/g$) are plotted across a concentration range determined as the mean concentration by each method of the six samples (low dust, dust SRM, low paint, high dust, high paint, and paint SRM). The logs of the variance for both paint and dust matrices were approximately equal, so it was deemed feasible to generate plots of reproducibility/repeatability for both matrices in the same regression. Paint and dust matrices were pooled to provide a useful concentration range for comparisons of repeatability and reproducibility. (This range would have been limited if paint and dust matrices were examined separately.) Plots for each method were prepared from a regression of the logs of repeatability/reproducibility versus the log of the method mean, then exponentiating to generate the plots. These plots are shown in Figures 1 and 2, and in Appendix G-8. The figures allow

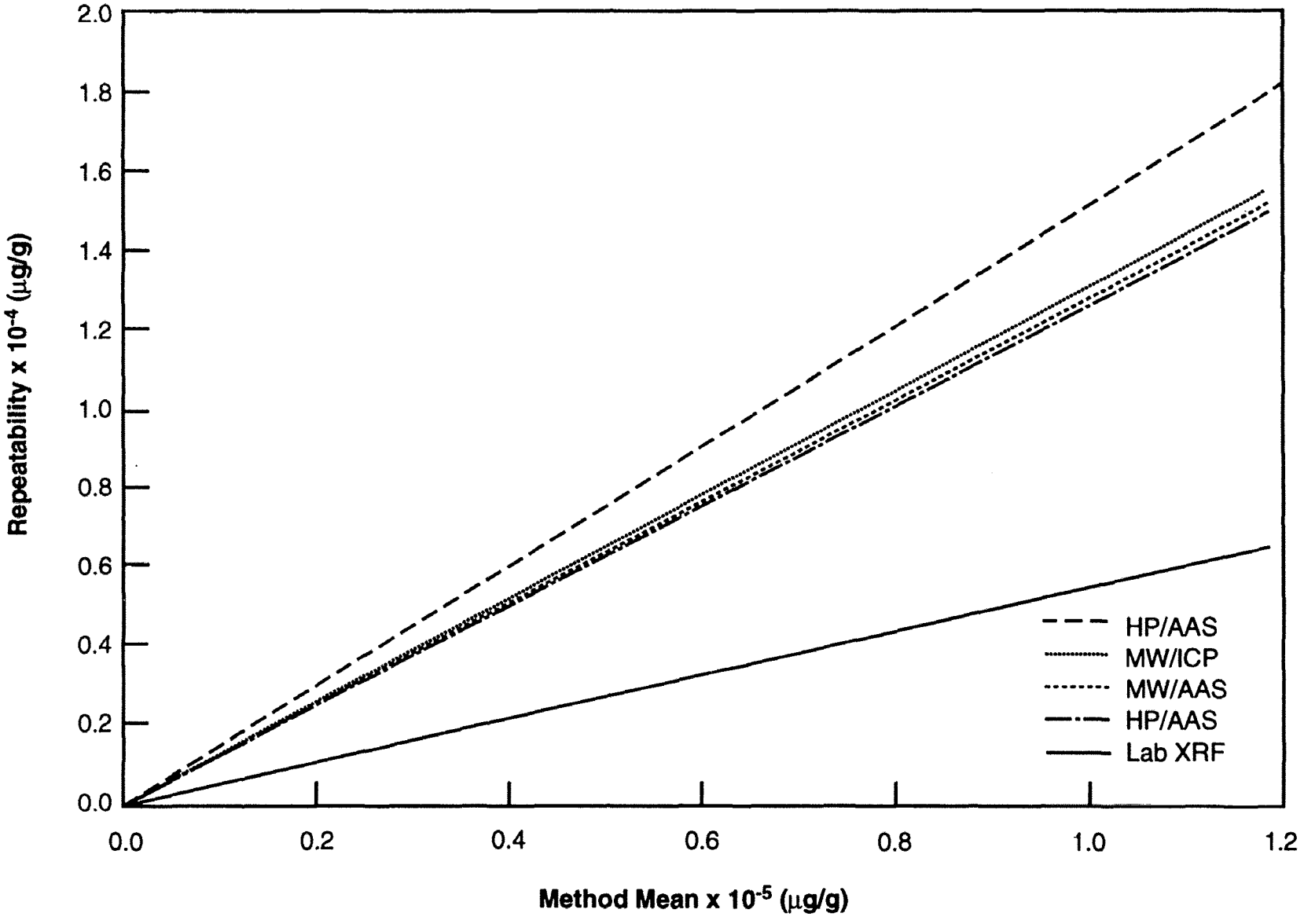

Figure 1. Repeatability versus lead concentration by method.

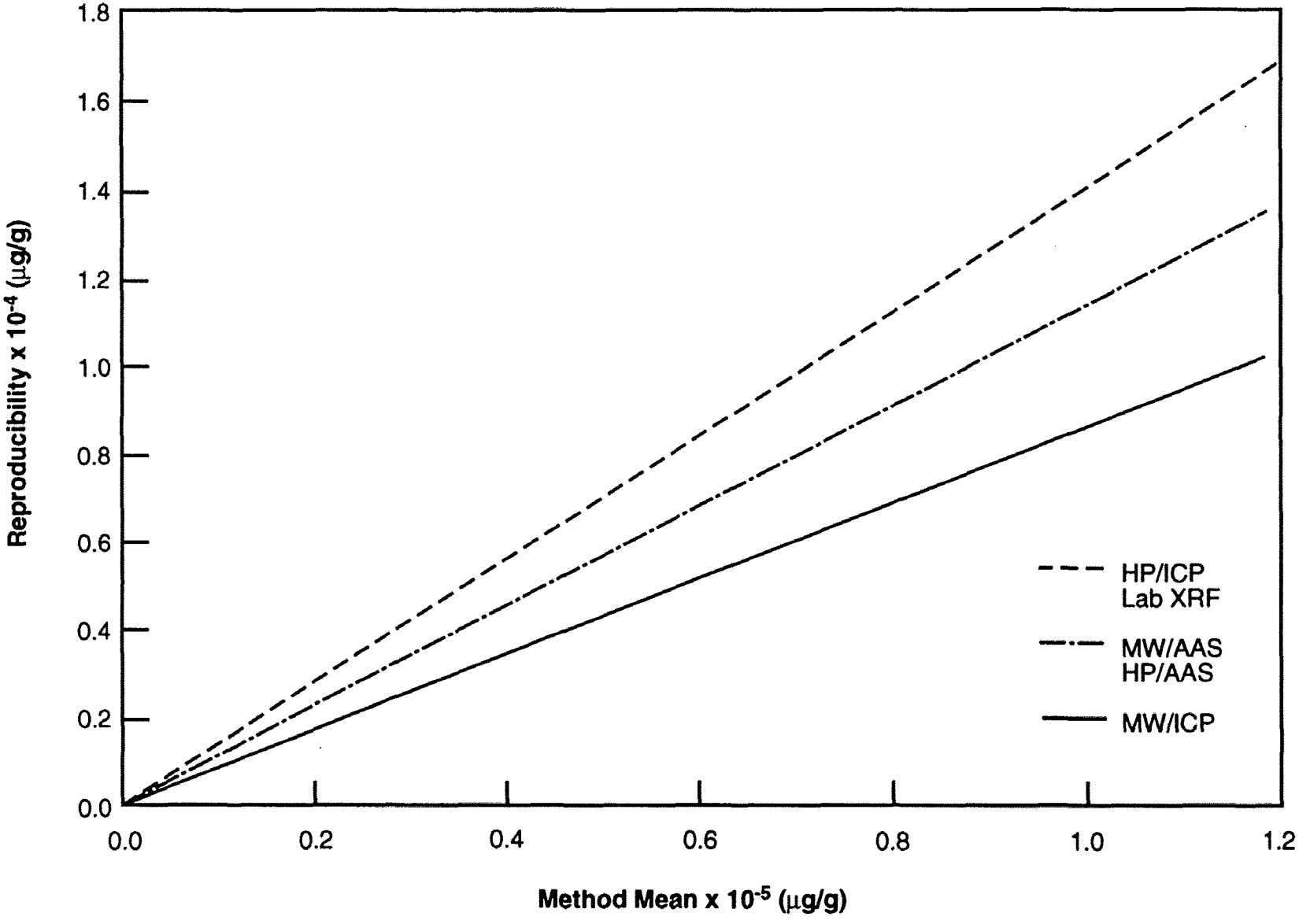

Figure 2. Reproducibility versus lead concentration by method.

a visual comparison of reproducibility and repeatability relative to concentration over the operating range of the methods. The regressions are forced through zero so that lines have a common origin; and the slopes, the change in repeatability or reproducibility per unit change in concentration, may be compared. The representations are a qualitative description, only; they are valid over the operating range of the method, but do not attempt to model the performance of the method at minimum detection. (Detection limits for the methods, presented in Table 8, were provided in the RTI Standard Operating Procedure[10] submitted to participating laboratories.)

Another representation of the variability is to pool the data over the concentration ranges and matrices to calculate overall repeatability and reproducibility by method. These data are provided in Table 9.

Figure 3 shows the 95% confidence intervals of the geometric mean recoveries (method mean/consensus mean) for the five methods examined. The six horizontal lines associated with each method represent the six samples, and thus, six concentration levels (SRM 1579, high paint, high dust, low paint, SRM 2711, and low dust) examined in the round robin. L, M, and U correspond to the low, mean, and upper limits of the 95% confidence interval, respectively. Plots of the geometric means by method are provided in Appendix G-9.

5.6 SAMPLE HOMOGENEITY

The round robin was designed to examine sample homogeneity using a two-way analysis of variance of logs for the blind duplicate MEM samples. Application of this method to the analysis treated sampling, analysis, and their interaction as random effects. For example, laboratories using the same method (MW/AAS, MW/ICP, HP/AAS, HP/ICP, or Laboratory XRF), and replicate samples selected from the same parent stock (P-1 and P-4; P-3 and P-5; D-1 and D-5; and D-2 and D-4; see Tables 4 and 5) were both viewed as random selections from a normal distribution. The assumption of random effects is appropriate in order to

Table 8. Instrumental Detection Limits for Lead
by Methods in the Round-Robin

Method	IDL[a]	MDL[b]
MW/AAS	0.1 μg/mL	20 μg/g
HP/AAS	0.1 μg/mL	100 μg/g
MW/ICP	0.05 μg/mL	10 μg/g
HP/ICP	0.05 μg/mL	50 μg/g
Laboratory XRF	3 μg/g	---

[a]Instrument Detection Limit - μg Pb/mL extracted solution

[b]Method Detection Limit - μg Pb/g matrix

Table 9. Repeatability and Reproducibility (%) by Method
Averaged across Matrices for Paint and Dust Samples
Submitted to Round-Robin Analysis

Method	Repeatability	Reproducibility
MW/AAS	10.7	13.7
HP/AAS	9.7	17.2
MW/ICP	10.5	11.7
HP/ICP	12.9	21.0
Lab XRF	4.8	19.4

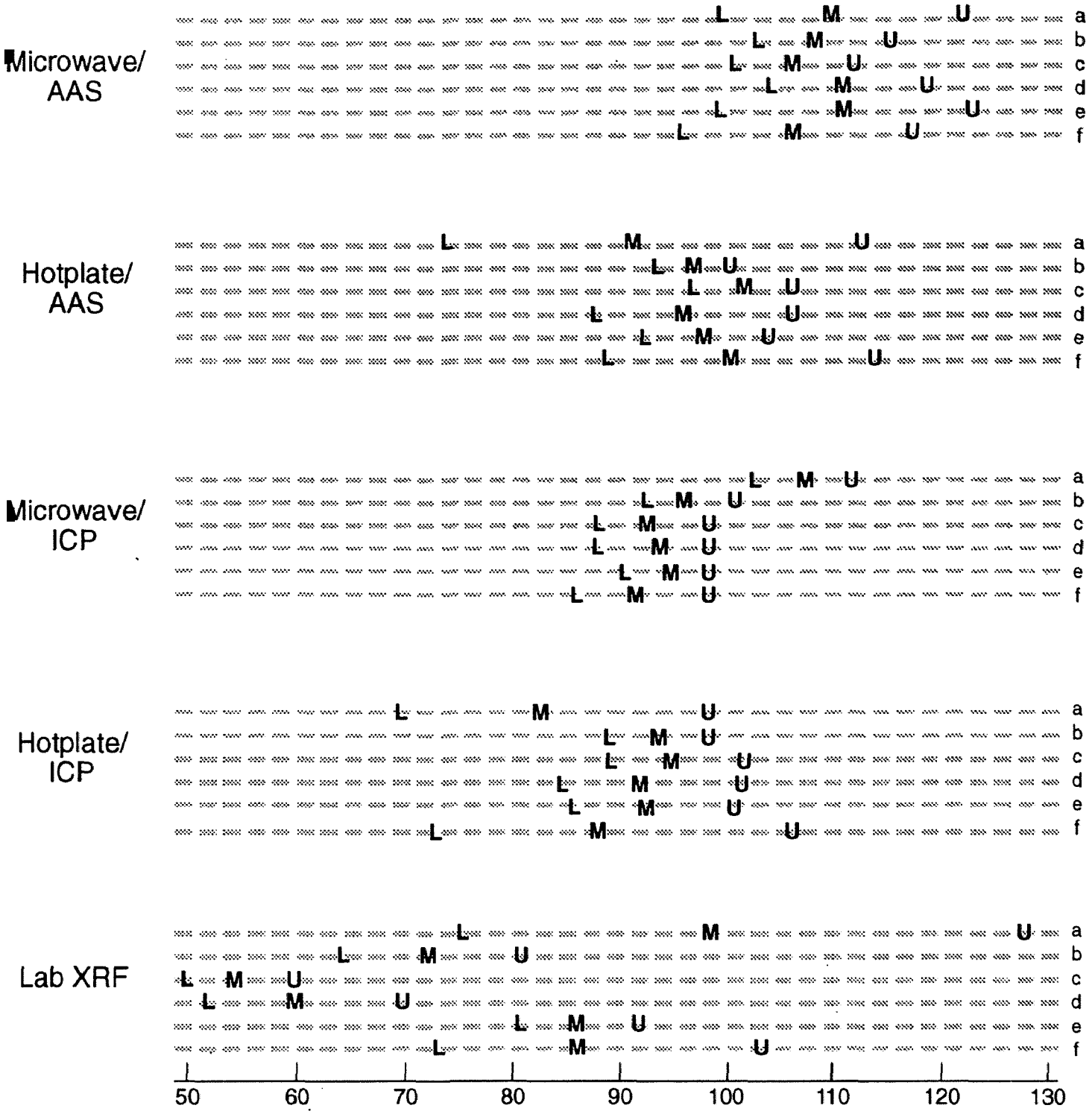

Figure 3. 95% Confidence Interval for the Geometric Mean Recovery (%) by Method.

LEGEND

a	Paint SRM 1579	108,826 µg/g	(Certified Value: 118,700 ± 400 µg/g)
b	High Paint	37,306 µg/g	
c	High Dust	4456 µg/g	
d	Low Paint	1676 µg/g	
e	Dust SRM 2711	1176 µg/g	(Certified Value: 1162 ± 31 µg/g)
f	Low Dust	104 µg/g	

95% Confidence Interval:
L – Lower limit
M – Mean
U – Upper limit

generalize results to a larger population of laboratories. This model was fit separately to all 20 combinations of method (5) by matrix (2) by level (2) for all the method evaluation materials.

A preliminary test for the absence of interaction or interdependence between sample and laboratory analysis indicated that this assumption was reasonable. Only one of twenty interaction tests was significant at the 5% level with this data set (low dust by MW/AAS: $0.025 < p < 0.5$). This is the expected number of rejections by chance alone, under the null hypothesis of no interaction. Accepting the hypothesis of no interaction means that the contributions of sampling and analysis to the total variance can be considered to be additive.

The two-way analysis of variance was applied to calculate the relative standard deviations (RSDs) for the samples. The RSD is equivalent to the difference in concentration between samples, expressed as percentage. In one case only (low dust by HP/ICP), the difference between samples was significant (8.9%). In all other cases, the sample-to-sample differences were less than 0.1% (16 out of 20 cases) or non-significant relative to the variance of the measurement method. On the average over the 20 cases, the sampling component of variance accounted for 1.37% of the total variance, with a 95% upper confidence limit for the sampling coefficient of variance being below 2.5%. It was, therefore, concluded that at the 95% confidence level, the concentrations of samples selected from the bulk materials were within 5% (between 95% and 105%) of the concentrations given as the consensus values. The RSD values are shown in Table 7.

The conclusion is that the bulk sample materials prepared by RTI were homogeneous, and that sample-to-sample variation did not significantly contribute to the analytical differences measured. According to criteria established in ISO Guide 35[17] (Appendix A-2), the method evaluation materials were considered "very homogeneous material."

5.7 PAIRWISE COMPARISON OF METHOD MEANS

Pairwise comparisons of method means within each of the six samples were performed using ordinary nonsimultaneous t tests at the 95% confidence level. There were ten possible paired comparisons of methods for each of the six samples (60 total comparisons), so three (5%) rejections of the null hypothesis were expected from chance alone. The results of the pairwise comparisons are presented in Table 10. The statistical comparisons indicated no declared differences for analysis of the low dust sample, and only two declared differences for the paint SRM. A total of 28 differences were declared; of these differences, 26 were associated with MW/AAS and Lab XRF, methods that generated extreme method means for five samples. Lab XRF gave the minimum mean for all samples except for the paint SRM. MW/AAS gave the maximum mean for all of the samples. This is a significant finding because the chance of equivalent methods generating a maximum or minimum result for 6 out of 6 samples is 0.000064. The statistical interpretation of the method effects is provided in Appendix G-10.

5.8 COMPARISON OF MEASUREMENTS BY ATOMIC ABSORPTION SPECTROMETRY AND INDUCTIVELY COUPLED PLASMA EMISSION SPECTROMETRY

As a part of RTI's earlier tasks in support of EPA programs for the analysis of lead in environmental matrices, RTI carried out method development studies for the analysis of lead by AAS and ICP. In these studies, low recoveries were found for the analysis of NIST SRM 1579 by ICP relative to analysis by AAS.[8] This bias was believed to be caused by ICP signal suppression from matrix effects associated with the paint samples. Because of these observations, RTI instructed the round-robin laboratories analyzing by ICP to dilute the paint and dust extracts into the 1 to 10 μg/mL range prior to analysis, and instructed AAS laboratories to use background correction, as specified in the SOP[10] (Appendix C-1, Sections 1.2.3.1.2, and 4.5.1) sent to the laboratories. Despite these instructions, the data

Table 10. Method Evaluation Materials and Standard Reference Materials Identified to Differ Significantly by Sample-Specific, Pairwise Comparison of Method Means Determined by Round-Robin Analysis

	Method			
	MW/AAS	HP/AAS	MW/ICP	HP/ICP
HP/AAS	Low Paint High Paint Dust SRM	---	---	---
MW/ICP	Low Paint High Paint High Dust Dust SRM	High Dust	---	---
HP/ICP	Low Paint High Paint Paint SRM High Dust Dust SRM	None	Paint SRM	---
Lab XRF	Low Paint High Paint High Dust Dust SRM	Low Paint High Paint High Dust Dust SRM	Low Paint High Paint High Dust	Low Paint High Paint High Dust

showed that AAS results were higher than ICP results for paint and dust samples by 3.5% to 18%, and 4.8 to 17%, respectively.

The difference in MW/AAS and MW/ICP results observed in the round-robin was investigated by digesting the round-robin test samples using a total digestion MW method and analyzing by ICP, with the addition of an internal standard. The method used for the total digestion was a combination of methods used by the U.S. Fish and Wildlife Service[23] and the Institute of Chemical Industry and Metallurgy of China.[24] (The RTI method and the reference methods[23,24] are provided in Appendix H.) The concentrations determined by this extraction/analysis method[23,24] were compared with the results reported for the MW extractions in the round-robin. The data are provided in Table 11. With the exception of the high dust sample, the concentrations measured by the total digestion MW/ICP method agreed closely with the round-robin MW/ICP results, but were consistently lower than the round-robin MW/AAS results. These data suggest that the difference in AAS and ICP results observed in the round-robin resulted from AAS signal enhancement, rather than ICP signal suppression. In fact, a review of instrumental parameter forms submitted by AAS laboratories indicated that a number of laboratories did not use background correction, a common source of positive bias, even though the SOP prescribed background correction for AAS measurements. This was considered a plausible explanation for the bias observed.

Table 11. Comparison of Method Means of Test Samples Submitted to Microwave Extraction Procedure Used in the Round-Robin with Concentrations Determined by a Total Microwave Digestion at RTI

Sample	Concentration of Lead (μg/g)			
	Round-Robin		Total Digestion (n=1)	
	MW/ICP (n=36)	MW/AAS (n=28)	MW/ICP*	MW/AAS
High Paint	36,654 $\pm$ 672	41,281 $\pm$ 1274	36,000	37,000
Low Paint	1603 $\pm$ 45	1896 $\pm$ 63	1620	1715
Paint SRM	118,281 $\pm$ 2476	122,432 $\pm$ 6507	118,700	121,000
High Dust	4281 $\pm$ 113	4847 $\pm$ 127	4960	4960
Low Dust	98 $\pm$ 3	114 $\pm$ 6	108	136
Dust SRM	1133 $\pm$ 24	1327 $\pm$ 72	---	---

*Concentrations corrected by addition of internal standard

SECTION 6.0
SUMMARY AND CONCLUSIONS

The round-robin study showed that the protocol used to prepare the paint and dust method evaluation materials provided homogeneous materials at targeted concentrations. The hypothesis of homogeneity was accepted in 19 out of 20 cases. (At the 95% confidence level, 1 rejection in 20 is expected by chance alone.) In 16 of the 20 cases, the sampling component of variance was less than 0.1; in 4 cases the sampling component was less than or equal to 10% of the total variance. On the average, the sampling component accounted for 1.37% of the total variance.

The five methods examined as a part of the round-robin study performed differently, with AAS methods producing results with a positive bias relative to ICP results. An explanation proposed for the bias was the absence or inadequate use of background correction by AAS laboratories. Results from analysis by Laboratory XRF were, in general, negatively biased relative to the results from the extraction methods. The quadratic tendency of the recovery data (excluding SRMs) suggested that an inadequate number of standards were provided for calibration. In addition, no standardized procedures for sample preparation or analysis were provided.

A pairwise comparison of method means declared the most differences in method means for the MW/AAS and laboratory XRF methods. The MW/AAS produced the highest mean for all six samples, whereas the laboratory XRF method produced the lowest mean for five of the six samples.

Laboratory XRF was the most repeatable of the methods, while HP/ICP results were the least repeatable. MW/AAS, MW/ICP, and HP/AAS methods produced results with similar repeatabilities. The MW/ICP method showed the best reproducibility for five of the six samples.

The results indicate the MW/ICP method to be a method of choice for the samples analyzed in the round-robin. This method gave good reproducibility

(total system coefficient of variation <12%), and showed the least variable recovery across concentrations.

SECTION 7.0
RECOMMENDATIONS FOR FURTHER STUDY

The study was successful because it provided the following:

- a protocol for the preparation of Method Evaluation Materials for lead-containing paint and dust,
- a means for validation of the protocol
  - at targeted concentrations, and
  - of acceptable homogeneity, and
- a means of comparing methods commonly used to analyze lead in environmental samples.

A number of questions about the differences in analytical methods were brought to light. Further studies are suggested to resolve questions that include the differences observed in AAS and ICP results, and the apparent negative bias observed for Laboratory XRF results.

An investigation of the apparent enhancement of AAS measurements relative to ICP may include the following:

- comparison of results for paint and dust reference materials by AAS analysis with and without background correction,
- comparison of ICP results of extractant solutions that are either:
  - diluted below concentrations specified in this round-robin (1 - 10 μg/mL), or
  - spiked with a solution of an internal standard, and
- development of a method for minimization of the enhancement/suppression effects.

The question of the apparent negative bias observed for Laboratory XRF results may be examined by the following:

- an investigation of matrix interference,
- the use of standardized protocols,
- the use of standardized materials for instrumental calibrations, and
- the use of internal standards.

SECTION 8.0

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Appendix A

Statistical Approach

Appendix A-1

Statistical Design of the Round-Robin

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ATMOSPHERIC RESEARCH AND EXPOSURE ASSESSMENT LABORATORY
RESEARCH TRIANGLE PARK
NORTH CAROLINA 27711

February 4, 1992

MEMORANDUM

SUBJECT: Review of RTI's Design of Round Robin for Lead in Paint and Dust

FROM: Jack Suggs
EDAB/EERD/AREAL (MD-77B)

TO: Sharon Harper

According to RTI's design, paint and dust solutions will be prepared at two different levels each--medium and high concentrations. Each of the two levels will be further split into two replicates. Each laboratory will receive 4 aliquots (2 reps x 2 levels) of paint solution and 4 aliquots of dust solution. In addition, each lab will receive a third "level" or standard reference material (SRM) of paint and of dust. The SRM's will not be replicated. Each laboratory will analyze in duplicate each of the aliquots using their method of analysis (XRF, AA, ICP). Methods AA and ICP also involve two extraction procedures: microwave and hotplate. The purpose of this study is to:

1. Evaluate the homogeneity of the paint and dust solutions prepared according to RTI's protocol

2. Estimate and compare between-lab differences

3. Estimate and compare within-lab differences

4. Compare methods of analysis.

A possible solution to these problems may be obtained through the use of linear models and the analysis of variance. Dust and paint data are treated separately but with the same model.

To avoid overparameterization in the models, think of the method/extraction combinations plus XRF as five different methods:

e.g. XRF AA/M AA/H ICP/M ICP/H

For each of these methods and each level of solution (including SRM), a separate analysis of variance can be performed.

e.g. Paint, Method = AA/H, Level = high

ANOVA TABLE

Source	DF	EMS	MS	F
Rep	1	$\sigma_D^2 + 2\sigma_{RL}^2 + 16\sigma_R^2$	MS_1	MS_1/MS_3
Labs	7	$\sigma_D^2 + 2\sigma_{RL}^2 + 4\sigma_L^2$	MS_2	MS_2/MS_3
Rep x Labs	7	$\sigma_D^2 + 2\sigma_{RL}^2$	MS_3	MS_3/MS_4
Duplicates	16	σ_D^2	MS_4	

All sources of variation are assumed random. The expected mean square (EMS) column shows the components of variation. These components may be estimated by equating the EMS to the mean square (MS) column. Also, certain F-ratios may be calculated (as suggested by the EMS) to test hypotheses corresponding to objectives in the design.

For example:

1) $F = MS_1/MS_3$

is used to test the hypothesis that the variation between replicate aliquots is zero. This is a test of the homogeneity of the solution,

2) $F = MS_2/MS_3$

is used to test the hypothesis that the difference between laboratories is not significant,

and 3) $F = MS_3/MS_4$

is used to test that the difference between replicate aliquots does not differ (in analysis) from lab-to-lab. This is compared to the variation between duplicates within each lab represented by σ_D^2.

For the SRM solution, the analysis of variance is less complicated since there are no replicate aliquots.

e.g.

Source	DF	EMS
Labs	7	$\sigma_D^2 + 2\sigma_L$
Duplicates	8	σ_D^2

In addition to tests of hypotheses, estimates of variance components σ_R^2 (between reps), σ_L^2 (between labs), σ_D^2 (between dups) can be obtained along with estimates of reproducibility standard deviations, and repeatability standard deviations defined by ASTM as

$$\text{Reprod} = (\sigma_L^2 + \sigma_D^2)^{1/2}$$

$$\text{Repeat} = \sigma_D.$$

By definition, two measurements made at a given level of solution using a given method by two different labs should not differ by more than 2.77 (Reprod) but 1 time in 20 due to chance alone. The value 2.77 (Repeat) applies to two measurements (duplicates) in the same lab.

These estimates can be obtained along with average values $\bar{X}$ for each solution level Med, High, SRM and each Method/extraction to produce the following table.

	Paint					Dust				
	XRF	AA/M	AA/H	ICP/M	ICP/H	XRF	AA/M	AA/H	ICP/M	ICP/H
Med	$\bar{X}$ = σ_R^2 = σ_L^2 = σ_D^2 = Reprod = Repeat =							Same		
High	$\bar{X}$ = σ_R^2 = σ_L^2 = σ_D^2 = Reprod = Repeat =							Same		
SRM	$\bar{X}$ = σ_R^2 = not retrievable σ_L^2 = σ_D^2 = Reprod = Repeat =							Same		

Using the entries in the table, the between-lab variances (σ_L^2), within-lab variances (σ_D^2), and between-rep variances (σ_R^2) can be examined for homogeneity across methods and levels. Averages can also be compared. If homogeneity is a fair assumption, the data may be pooled into a more complex analysis. This is not really necessary, but a layout of the sources of variation and degrees of freedom for the full model helps to identify the many different comparisons.

e.g., Paint, medium and high levels (no SRM)

	Source	df
Homogeneity of solution	Levels	1
	Reps	1
	Levels x Reps	1
Method comparison	Methods	4
	Level x Methods	4
	Rep x Method	4
	Level x Rep x Method	4
Between-lab variation	Lab (Method)	=35
	Level x Lab (Method)	=35
	Level x Rep x Lab (Method)	=35
Within-lab	Duplicates	152
	Total	287

Another possible analysis of the data would involve only the AA and ICP methods. These methods each have two extraction procedures. The layout of the analysis of variance for paint (or dust) at two prepared levels (no SRM) would look something like the following.

	Source	df
Homogeneity of solution	Level	1
	Rep	1
	Level x Rep	1
Method comparisons	Method (i.e. AA vs ICP)	1
	Extract. (i.e. Micro vs Hot)	1
	Meth x Extract	1
	Level x Meth	1
	Level x Meth x Extract	1
	Rep x Method	1
	Rep x Extract	1
	Rep x Meth x Extract	1
	Level x Rep x Meth	1
	Level x Rep x Extract	1
	Level x Rep x Meth x Extract	1
Between-lab variation	Lab (Meth x Extract)	≈29
	Level x Lab (Meth x Extract)	29
	Rep x Lab (Meth x Extract)	29
	Level x Rep x Lab (Meth x Extract)	29
Within-lab	Duplicates	100
	Total	231

Most of the interactions, especially the higher-order interactions, will probably be zero. In any case, the 3- and 4-way interactions are difficult to interpret and should probably be combined to provide denominators for F-tests of single and 2-way interactions.

These are simply suggestions for analysis based on the proposed design. I'm sure there are other possible approaches. There are two ways that more balance could be achieved: 1) more labs for AA/microwave, 2) replicate aliquots for the SRMs. I know that this last suggestion is prohibited by cost, but it would provide a comparison of the homogeneity within an SRM as compared to the prepared materials.

cc: W. J. Mitchell

Appendix A-2

ISO Guide 35

GUIDE 35

Certification of reference materials — General and statistical principles

Second edition 1989

Contents

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

ISO guides are intended essentially for internal use in ISO committees or in some cases for the guidance of member bodies when dealing with matters that would not normally be the subject of an International Standard.

ISO Guide 35 was drawn up by the ISO Committee on reference materials (REMCO) and was submitted directly to ISO Council for acceptance. This second edition cancels and replaces the first edition (ISO Guide 35 : 1985), to which a new clause 9 has been added.

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Printed in Switzerland

Certification of reference materials — General and statistical principles

Introduction

The Committee on reference materials (REMCO) is concerned with guidelines for the preparation, certification and use of reference materials. This Guide is intended to describe the general and statistical principles for the certification of reference materials.

Various sections of this Guide were prepared by different delegates to REMCO. The project was co-ordinated with representatives of ISO/TC 69, *Applications of statistical methods*.

Acknowledgment is given to J. D. Cox (BSI, UK) for preparation of the section on the role of reference materials in measurement systems (clause 3). Much of clauses 4, 5 and 6 is based on material contained in three previously published sources:

a) CALI, J.P. *et al.* The role of standard reference materials in measurement systems, *NBS Monograph 148*, Washington, DC, National Bureau of Standards, 1975 (especially Chapter III, by H. H. Ku);

b) URIANO, G. A. and GRAVATT, C. C. The role of reference materials and reference methods in chemical analysis. *Crit. Rev. in Anal. Chem.* 6 1977 : 361;

c) MARSCHAL, A. *Matériaux de référence*. Bureau National de Métrologie, Laboratoire National d'Essais, Paris.

K. R. Eberhardt (ANSI, USA) prepared clause 7 on the use of a definitive method to certify reference materials. R. Sutarno and H. Steger (SCC, Canada) prepared clause 8 on the use of an interlaboratory testing programme to certify reference materials. H. Marchandise (Community Bureau of Reference, Commission of the European Communities) prepared clause 9 on a metrological approach to certification, included for the first time in the second edition of this Guide. G. Uriano (ANSI, USA) served as editor of the Guide.

Special acknowledgement is given to members of ISO/TC 69/SC 6 and its Secretary K. Petrick (DIN, Germany, F.R.), for their co-operation in preparing those sections of the document concerned with the statistical analysis of data. In particular the many contributions of Prof. P. T. Wilrich (DIN, Germany, F.R.) and Dr. T. Miyazu (JISC, Japan) of ISO/TC 69/SC 6 to the review and editing of the Guide are gratefully acknowledged.

Earlier Guides[1-3] prepared by REMCO have dealt with the following aspects of reference materials:

a) mention of reference materials in International Standards;

b) terms and definitions used in connection with reference materials;

c) the contents of certificates of reference materials.

The purpose of this Guide is to provide a basic introduction to concepts and practical aspects related to the certification of reference materials. ISO Guide 33[29] more fully addresses concepts and practical aspects related to the use of reference materials.

1 Scope

According to the definition given in 2.1, reference materials (RMs) may be used in diverse measurement roles connected with instrument calibration, method assessment and assignment of property values. The purpose of clause 3 is to discuss these measurement roles and to show how traceability[1] of measurement may be secured by use of RMs, thus yielding worldwide compatibility of measurement.

Just as certified reference materials (CRMs) are to be preferred over other classes of RMs in citations in International Standards[11], so also are CRMs to be preferred over other classes of RMs in measurement science generally, given that CRMs needed for a particular type of measurement exist. Assistance in locating the source(s) of supply of CRMs for various technical fields is afforded by ISO's *Directory of certified reference materials*[14].

It will be evident that the quality of a measurement based on use of a CRM will depend in part on the effort and care expended by the certifying body on determining the property

1) An internationally agreed definition of "traceability" in measurement science is given in reference [5]:

traceability: The property of a result of a measurement whereby it can be related to appropriate standards, generally international or national standards, through an unbroken chain of comparisons.

value(s) of the candidate CRM. Hence the process of certification[2] should be carried out using well-characterized measurement methods that have high accuracy as well as precision and provide property values traceable to fundamental units of measurement. Furthermore, the methods should yield values with uncertainties that are appropriate to the expected end-use of the CRM. Clauses 4 and 5 deal with two of the most important technical considerations in the certification of RMs — measurement uncertainties and material homogeneity. Clause 6 provides general principles for RM certification.

Two commonly used general approaches to assuring technically valid RM certification are discussed in clauses 7 and 8. Clause 7 describes the use of a single method of the highest accuracy (i.e. sometimes referred to as a "definitive" or "absolute" method) and usually employed by a single laboratory for RM certification. Clause 8 describes the use of an interlaboratory testing approach to RM certification, which might involve more than one method.

The metrological approach discussed in clause 9 has as its objective the production of certified values the accuracy and uncertainty of which are demonstrated by experimental evidence.

In summary, the purpose of this Guide is to assist in understanding valid methods for the certification of RMs and also to help potential users to better define their technical requirements. The Guide should be useful in establishing the full potential of CRMs as aids to assuring the accuracy and interlaboratory compatibility of measurements on a national or international scale.

2 Definitions

Definitions of the basic terms "reference material" and "certified reference material" were first put forward in 1977[1] and were later amended slightly[2] to read as follows.

2.1 reference material; RM: A material or substance one or more properties of which are sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials.

NOTE — An RM may be in the form of a pure or mixed gas, liquid or solid, or even a simple manufactured object. Some RMs are certified in a batch, any reasonably small part of which should exhibit the property value(s) established for the whole batch within stated uncertainty limits. Other RMs exist as individually manufactured objects which are also certified individually. Numerous RMs have properties which, because they cannot be correlated with an established chemical structure or for other reasons, cannot be measured in mass or amount of substance units or determined by exactly defined physical or chemical measurement methods. Such RMs include certain biological RMs (for example a vaccine to which an international unit has been assigned by the World Health Organization) and certain technological RMs (for example rubber blocks for the determination of abrasiveness or steel plates for the determination of hardness). It is recognized that the definition of "reference material" given above could involve an overlap with the term "material measure" as defined in the *International Vocabulary of Basic and General terms in Metrology*[6]; consequently, some materials may be characterized as either reference materials or material measures.

2.2 certified reference material; CRM: A reference material one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation which is issued by a certifying body.

NOTE — A CRM may consist of units which are each certified individually or which are certified by examination of representative samples from a batch.

3 The role of reference materials in measurement science

Metrology is the field of knowledge concerned with measurement. Metrology or measurement science [1] includes all aspects both theoretical and practical with reference to measurements, whatever their level of accuracy, and in whatever fields of science or technology they occur[6]. This clause describes the role of reference materials in quantitative measurements.

3.1 The role of reference materials in the storage and transfer of information or property values

By definition (2.1), a reference material has one or more properties, the values of which are well established by measurement. Once the property value(s) of a particular RM have been established, they are "stored" by the RM (up to its expiration date) and are transferred when the RM itself is conveyed from one place to another. To the extent that the property value of an RM can be determined with a well-defined uncertainty, that property value can be used as a reference value for intercomparison or transfer purposes. Hence RMs aid in measurement transfer, in time and space, similar to measuring instruments [2] and material measures[6].

A general scheme for constructing a hierarchical measurement system is illustrated in section 6.5 of the *Vocabulary of Legal Metrology*[6]. The interlinking of various levels and stations within a measurement system via "reference standards" may, in principle, be effected by either measuring instruments or material measures or RMs.

An RM must be suitable for the exacting role it performs in storing and transferring information on measured property values. The following technical criteria (legal or commercial criteria

1) "Measurement science" is therefore synonymous with "metrology" according to the international definition of the latter term[6]; it should be noted, however, that current usage generally restricts the term "metrology" to physical measurements at high accuracy. The term "metrology" is, however, being increasingly used in the context of chemical, engineering, biological and medical measurements.

2) Some measuring instruments are not readily movable (by reason of size, mass, fragility, instability or cost), in which case the measurand must be brought to the instrument to effect the measurement transfer. But all RMs and material measures are readily movable and thus can be taken to the measurand.

may be relevant also) apply to the fitness for purpose of RMs in general:

a) the RM itself and the property value(s) embodied in it should be stable for an acceptable time-span, under realistic conditions of storage, transport and use;

b) the RM should be sufficiently homogeneous that the property value(s) measured on one portion of the batch should apply to any other portion of the batch within acceptable limits of uncertainty; in cases of inhomogeneity of the large batch, it may be necessary to certify each unit from the batch separately;

c) the property value(s) of the RM should have been established with a precision and an accuracy sufficient to the end use(s) of the RM;

d) clear documentation concerning the RM and its established property value(s) should be available. Preferably the property value(s) should have been certified, so the documentation should then include a certificate, prepared in accordance with ISO Guide 31 [3].

The word "accuracy" was advisedly used in c) to indicate that whenever possible, the measurement of a given property value should have been made by a method having negligible systematic error or bias relative to end-use requirements (or where the result has been corrected for a known bias) and by means of measuring instruments or material measures which are traceable to national measurement standards. Subsequent use of an RM with traceable property values ensures that traceability is propagated to the user. Since most national measurement standards are themselves harmonized internationally, it follows that measurement standards in one country should be compatible with similar measurements in another country. In many cases, CRMs are appropriate for the intercomparisons of national measurement standards.

3.2 The role of reference materials in the International System of units (SI)

3.2.1 Dependence of the SI base units on substances and materials

The majority of measurements made in the world today are within the framework of the International System of units [7]. In its present form, SI recognizes seven base units, namely the units of length (metre, symbol m), mass (kilogram, kg), time (second, s), electric current (ampere, A), thermodynamic temperature (kelvin, K), amount of substance (mole, mol) and luminous intensity (candela, cd). The definitions [7] of these base units mention the following substances: krypton-86 [1] (for defining the metre), platinum-iridium (for fabricating the prototype kilogram), caesium-133 (for defining the second), water (for defining the kelvin) and carbon-12 (for defining the mole). Opinions differ as to whether the substances named fall under the definition of reference material (2.1). The use of these substances in basic metrology is consistent with the use of reference materials in other types of measurement applications. Certainly such materials have a special status as defined substances on which the SI is based. The dependency strictly applies to definition of the unit, since realization of the units may involve other substances/materials. This is especially true in regard to the realization of the mole [8] and the kilogram.

3.2.2 The realization of derived SI units with the aid of reference materials

From the seven base units an unlimited number of derived units of the SI are obtainable by combining base units as products and/or quotients. For example, a derived unit of mass concentration is defined as $kg \cdot m^{-3}$ and the derived unit of pressure (given the special name pascal, symbol Pa) is defined as $m^{-1} \cdot kg \cdot s^{-2}$. Formally speaking, the derived units ultimately depend on the substances on which the base units themselves depend (see 3.2.1). In practice, the derived units are often realized not from base units but from RMs with accepted property values. Thus a variety of substances/materials may be involved in the realization of derived units (examples 1 and 2 below) or even of base units (examples 3 and 4 below).

Example 1: The SI unit of dynamic viscosity, the pascal second ($Pa \cdot s = m^{-1} \cdot kg \cdot s^{-1}$) may be realized [9] by taking the value for a well purified sample of water as 0,001 002 Pa·s at 20 °C.

Example 2: The SI unit of molar heat capacity, the joule per mole·kelvin ($J \cdot mol^{-1} \cdot K^{-1} = kg \cdot m^2 \cdot s^{-2} \cdot mol^{-1} \cdot K^{-1}$) may be realized [10] by taking the value for purified α-alumina as 79,01 $J \cdot mol^{-1} \cdot K^{-1}$ at 25 °C.

Example 3: The SI unit of amount of substance, the mole, may be realized by taking 0,069 72 kg of highly purified gallium metal [11].

Example 4: The SI unit of temperature, the kelvin, may be realized at any temperature T_1 ($273,15\ K < T_1 < 903,89\ K$) from measurements of the resistance of a highly pure platinum wire at T_1, at the triple point of purified water, at the freezing point of purified tin and at the freezing point of purified zinc, coupled with use of a specified mathematical relation [12]. The word "thermodynamic" has been deliberately omitted here to avoid controversy over whether thermodynamic temperatures are, or are not, the same as International Practical Temperatures of 1968: the intention of the International Committee for Weights and Measures was to match the two sorts of temperature exactly, within the framework of knowledge available during 1968-1975.

3.2.3 Connection of analytical chemistry to the International System of units

It will be noted that purified (often called "pure") chemical substances were cited in each of the examples 1 to 4 (3.2.2). The measurement of degree of purity, or more generally of the chemical composition of materials, is within the realm of analytical chemistry. In addition to the dependence of SI on chemical substances, the dependence of analytical chemistry on SI is worthy of examination. Presently, most analytical

1) Recently, the General Conference on Weights and Measures redefined the metre as the distance travelled by light in a vacuum during 1/299 792 458 of a second.

chemists employ units within the SI (all base units except the candela and also many derived units) in their measurements. However, compositional analysis depends on an additional concept, namely that pure chemical species exist to which the chemical compositions of other substances and materials are referred, by invoking the laws of chemical change and stoichiometry.

From one or more pure chemical species, considered to be primary measurement standards, it is feasible to construct measurement hierarchies for analytical chemistry similar to those used in physical measurement[6]. Examples of such measurement standards are:

a) the electron, to which other species can be connected by electrochemical analysis[13];

b) carbon-12, to which other species can in principle be connected by mass spectrometry, Raoult's law measurements, or volumetric measurements with low-density gases, etc.;

c) a highly purified element or compound, to which other species can be connected by electrochemical, gravimetric, titrimetric, spectrometric methods, etc.

The "other species" cited in these examples will in many cases be used as RMs. Many substances can fill this role of intermediaries between primary and working analytical standards using the diversity of techniques and chemical reactions that an analyst may employ. The concept of traceability applies to analytical chemistry as much as it does to other branches of measurement science. The quality of the result of a chemical analysis will be enhanced if the result's traceability can be clearly stated in terms of the traceability of the instruments, material measures and RMs employed. In most cases, the traceability will also depend on the values of the relative atomic masses (formerly called "atomic weights") used in the calculations; the source of these should be recorded by the analyst (for example [11]).

3.2.4 The role of reference materials in realizing units outside of the SI

Where the components of a measurement system (for example the Imperial system) can be related exactly to the corresponding components of the SI, it is unnecessary to have independent means for realizing the non-SI measurement system. Where the quantities cannot be related to those of the SI, then independent realization of the non-SI units is in principle necessary. In practice, however, few such systems remain in use and thus are mostly historical curiosities.

3.3 Use of reference materials

REMCO intends to publish a separate guide covering general and statistical principles for the use of reference materials. There are very few published documents that address general problems associated with the use of reference materials. The reader is referred to the documents and recommendations published by IUPAC Commission I.4 on Physico-chemical Reference Materials and Standards, which deal primarily with the use of reference materials for realization of physical properties. The following IUPAC Commission I.4 publications in *Pure and Applied Chemistry* are concerned with the certification and use of reference materials for physical properties:

Physical property	Volume, date of publication and page number
Enthalpy	40 1974 : 399
Optical rotation	40 1974 : 451
Optical refraction	40 1974 : 463
Density	48 1976 : 1
Relative molecular mass	48 1976 : 241
Absorbance and wavelength	49 1977 : 681
Reflectance	50 1978 : 1 477
Potentiometric ion activities	50 1978 : 1 485
Viscosity	52 1980 : 2 393
Permittivity	53 1981 : 1 847
Thermal conductivity	53 1981 : 1 863

4 Measurement uncertainty

In discussing measurement uncertainties, the terms "precision", "systematic error or bias", and "accuracy" are usually used. The meanings of these terms are not rigidly fixed, but depend to a large extent on the interpretation and use of the data[14, 15].

4.1 An illustrative example

If two equally trained operators, A and B, each make four replications of a measurement on a uniform material each day for 4 days on one instrument, and 4 days again on a similar instrument, the results, 16 sets of four measurements, may look like those in figure 1. What can be seen from this plot ?

a) the spreads among each set of four values are comparable, perhaps slightly smaller for instrument 2 than instrument 1;

b) there appears to be more variability between daily results than within sets of daily results, particularly for instrument 1;

c) operator B gives lower results than operator A;

d) instrument 1 gives lower results than instrument 2.

Figure 1 is constructed for the purpose of demonstration, and actual measurements could be better or worse than shown. However, this plot does show some four types of factors that contributed to the total variability of these measurements:

1) factors acting within days;

2) factors acting between days;

3) factors due to instrument systems;

4) factors due to operators.

Appropriate techniques are available for the separate estimation of the effects of these four factors and standard deviations could be computed corresponding to each of them. However, the limited number of operators and instruments prevents the computation of standard deviations as reliably for

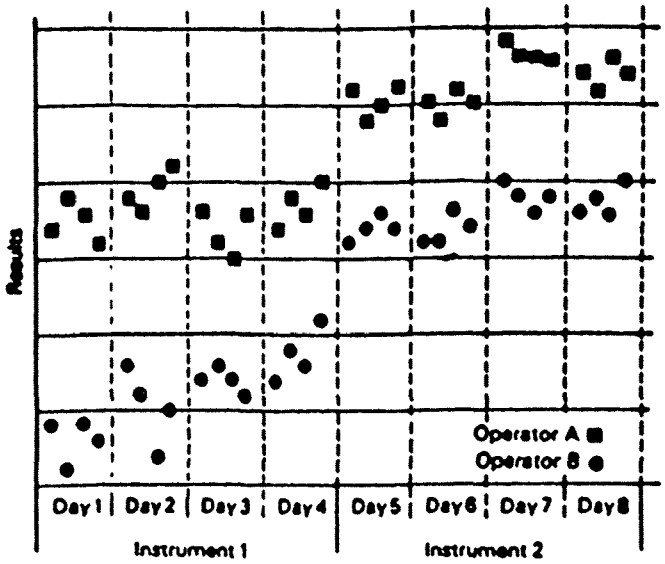


Figure 1 — An example of results of measurements by two operators using two instruments on eight different days

factors 3) and 4) as for factors 1) and 2). The time and work involved certainly impose limits on any efforts to do so.

The failure to allow for factors relating to instruments and operators is one of the main causes for the unreasonable differences usually encountered in interlaboratory, or round-robin, types of tests [16]. Because instruments vary from time to time and operators change, the result from a laboratory at a given time represents only one of the many results that could be obtained, and the variability caused by these two sources must be considered as part of the precision of the laboratory. The standard deviation computed without regard to these effects would underestimate the true variability.

If, by the proper use of standards and reference methods [17], these two sources of errors were eliminated, the standard deviation computed from the 16 means of sets of four measurements would be the proper measure of precision. Presumably the grand mean of the 16 mean values would be reported.

The mean of many values is more stable than individual measurements. When extraneous sources of variation, such as instrument and operator effects, are eliminated, the relationship between the standard deviation of individual measurements and the standard deviation of the mean of n such measurements can be expressed as

$$\sigma(\bar{X}_n) = \frac{\sigma(X)}{\sqrt{n}} \qquad \ldots (1)$$

In other words, the standard deviation of the mean is smaller than the standard deviation of individual measurements by a factor of $1/\sqrt{n}$. One important provision must hold for this relationship to be true, i.e. that the n measurements are independent of each other. "Independence" can be defined in a probability sense, but for present purposes, measurements may be considered independent if they show no trend or pattern. This is certainly not true in figure 1, and to say that the standard deviation of the mean of all 64 values is 1/8 ($= 1/\sqrt{64}$) of the standard deviation of individual measurements would seriously underestimate its true variability. Moreover, the relationship in equation (1) is expressed in terms of the true value of the standard deviation, σ, which is usually not known. As the computed standard deviation, s, is itself an estimate of σ from the set of measured values, the standard deviation of the mean in equation (1) is only approximated when s is used in place of σ.

The use of the standard deviation computed from daily averages rather than individual values is preferred because the former property reflects a component of variability between days, or over time, which is usually present in precision measurement.

4.2 Some basic statistical concepts

The basic information available on the measurement errors is summarized by:

a) the number of independent determinations or the number from which a mean was computed and reported;

b) an estimate of the standard deviation, s, defined by

$$s = \left[\frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x})^2\right]^{1/2}$$

where n measurement results are denoted by $x_1, x_2, \ldots, x_n$, and their mean is

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$$

From a) and b) several useful derived statistics can be computed:

c) standard deviation of the mean of n measurements

$$s(\bar{x}_n) = \frac{s}{\sqrt{n}}$$

This is sometimes called the standard error of the mean to differentiate it from the standard deviation of individual determinations.

NOTE — As n becomes large, the value of $s(\bar{x}_n)$ becomes very small, showing that the average of a large number of measurements approaches a constant value μ which is usually the objective of the measurement procedure.

d) confidence interval for the mean (normal distribution). Each time n measurements are made, a value of the average of the measurements is reported. These averages will differ from time to time within certain limits. Assuming a normal distribution, one interval of the type $\bar{x} \pm \delta$ can be constructed [18] such that the interval from $\bar{x} - \delta$ to $\bar{x} + \delta$ will

be fairly certain to include the value of μ desired. The interval is computed by:

$$\delta = t \frac{s}{\sqrt{n}} \qquad \ldots (2)$$

where t is a tabular value of the Student distribution, and depends on the confidence level and the degrees of freedom for s;

e) 2-sigma (or $2s$), 3-sigma (or $3s$) limits. These limits describe the distribution of measurement error. If a measurement is made by the user of a CRM having the same precision (i.e. same σ) as that obtained by the certifying laboratory, his measurements should fall (with probability approximately 0,95 to 0,997) within these limits when σ is well-established. Otherwise there is evidence of systematic difference.

4.3 Instrument and operator errors

Instrument and operator types of errors have not yet been treated. An ideal situation would be to eliminate them from the measurement process, or to use more instruments and more operators and then estimate standard deviations associated with these sources. When neither of the above is feasible or practical, the least that can be done is to use two instruments and/or operators. If the confidence intervals for the mean results of the two instruments do not overlap, then there is good evidence of instrument difference.

Using his experience and judgement, a measurement scientist may arrive at reasonable bounds for these types of errors. If the bound is not computed from measurement data, then its validity cannot be supported by statistical analysis. In such cases, these bounds are "guesstimates" and the only recourse is to treat them as limits to systematic errors.

The detection of differences and the separation of the total variability into its identifiable components can be facilitated through careful planning and statistical design of the experiment.

4.4 Differences among measurement methods

Each measurement method purports to measure the desired property of a material, but seldom does a method measure the property directly. In most cases the method actually measures some other property that is related to the property by theory, practice, or tradition, and then converted to the value of the desired property through these relationships. Discrepancies among results of different measurement methods are common, even for measurements leading to the determination of fundamental physical constants[19].

In the preparation of a CRM, usually two or more measurement methods are employed for each property measured. If these methods are well established by virtue of past experience, the results yielded by these methods usually agree to within the uncertainty assigned to each method.

In a few cases these differences are so large that the results cannot be reconciled, and these results are then reported separately for each individual method. The RM is either not certified or certified on a method-dependent basis. A historical example of this type of reporting is NBS CRM 1091, Stainless Steel. The nitrogen content was measured by vacuum fusion and pressure bomb-distillation, and gave results of 861 and 945 mg/kg, with standard deviations of 3 and 20 mg/kg, respectively. Clearly one or both methods have a systematic error that is large compared to the variability of material or the measurement uncertainty. A report of the average of the two methods would be highly misleading.

Measurement accuracy in its absolute sense is never realized. In practice, certified values of some reference materials are defined by using a referee method or assigning a value by a well-defined procedure so that at least the same benchmark will be used by everyone in the field. The importance of reference methods to supplement the use of these measurement standards is also being emphasized[17]. A good example is the reference method for blood haemoglobin and the value assigned as a benchmark to the reference material issued by the International Committee for Standardization in Hematology (ICSH)[20, 21].

4.5 Uncertainties of certified values

The uncertainty of a CRM value is usually made up of several components, some supported by data and some not:

a) a statistical tolerance interval giving bounds to material inhomogeneity based on data and statistical computations;

b) a confidence interval for the mean giving bounds to measurement error based on data and statistical computations;

c) components of measurement uncertainty due to variation among laboratories and/or operators and measurement methods;

d) a combination (addition of absolute values or the square root of the sum of the squares) of estimated bounds to "known" sources of possible systematic error based on experience and judgement (in other words, there are no data, or an insufficient number of data, to make a statistical calculation).

The word "known" is quoted above to contrast with systematic errors that are "unknown" or unsuspected. These unsuspected errors could occur in a number of ways – a component in the physical system, a minor flaw in the theoretical consideration, or the rounding error in a computation. As more homogeneous materials become available, and more precise measurement methods are developed, these types of errors will be detected by design or by chance and hopefully will be eliminated. Improved accuracy in the measurement of a property is basically an expensive iterative process and unwarranted demand for accuracy could mean the waste of resources.

4.6 Statements of uncertainty on CRM certificates

A variety of statements of uncertainty can be found in past and current certificates issued for CRMs around the world. Some of these statements are well formulated and supported by data,

others are not; some of these statements contain a wealth of information that is useful to exacting users, but overwhelming to others; some statements are oversimplified with a resulting loss of information. Because the originator of a CRM has to keep all classes of users in mind, the use of a single form of statement is not usually possible. The intention is that all these statements are unambiguous, meaningful, and contain all the information that is relevant for potential users.

Some commonly used statements, taken from existing certificates, are listed in 4.6.1 to 4.6.4.

4.6.1 Example 1: 95 % confidence limits for the mean

Rubidium chloride

Absolute abundance ratio ..... 2,593 ± 0,002

"The indicated uncertainties are overall limits of error based on 95 % confidence limits for the mean and allowances for the effects of known sources of possible systematic error."

Because the isotopic ratio is a constant for a given batch of material and is not subject to errors of material inhomogeneity, the 95 % confidence limits for the mean refer to measurement error only. This is computed from

$$t \frac{s}{\sqrt{n}}$$

as described in equation (2).

The effects of known sources of possible systematic error are discussed in detail in "Absolute isotopic abundance ratio and atomic weight of terrestial rubidium"[22].

4.6.2 Example 2: 2-sigma or 3-sigma limits

Glass Filters for Molecular Absorption Spectrometry

Absorbance ..... 0,500 0 ± 0,002 5

"This uncertainty is the sum of the random error of ± 0,1 % relative (2σ limit) and of estimated biases which are ± 0,4 % relative."

Each glass filter was individually calibrated, and the standard deviation refers to measurement error, including the cleanliness of the surface. As these glass filters will be used time after time, a multiple of the standard deviation is a proper measure of variability.

4.6.3 Example 3: Uncertainty expressed in significant digits

AISI 4340 Steel

Element Mass Fraction

Carbon ..... $3,8_2 \times 10^{-3}$

Manganese ..... $6,6 \times 10^{-3}$

According to the explanation given in the text: "The value listed is not expected to deviate from the true value by more than ± 1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ± 5." Thus, the mass fraction of carbon, expressed as a percentage, is between 0,377 and 0,387; and that for manganese is between 0,65 and 0,67. These uncertainties include material inhomogeneity, measurement imprecision, and possible bias between laboratories and implicit rounding, because these values are "... the present best estimate of the true value based on the results of a co-operative interlaboratory analytical programme."

When 20 to 30 elements are to be certified for one material, this method gives a concise and convenient summary of the results. As these limits are expressed in units of 5 and 10, some information is unavoidably lost for some of the elements. However, when the certified value is used, it is important to use all of the digits given including the subscripts. The uncertainty stated on this certificate depends heavily on the use of chemical judgement.

4.6.4 Example 4 : Standard deviation, and number of determinations

Method		Oxygen in ferrous metals (µg/g)		
		CRM A (Ingot iron)	CRM B (Stainless steel : AISI 431)	CRM C (Vacuum melted steel)
Vacuum fusion				
	$\bar{x}$	484	131	28
	s	14	8	2
	n	216	286	105
Neutron activation				
	$\bar{x}$	492	132	28
	s	28	7	4
	n	6	6	5
Inert gas fusion				
	$\bar{x}$	487	129	29
	s	13	8	5
	n	12	11	20

where

$\bar{x}$ is the mean oxygen value;

s is the standard deviation of an individual determination;

n is the number of determinations.

NOTE — The standard deviation includes error due both to the imprecision of the analytical method and to possible heterogeneity of the material analysed.

One criticism against this mode of presentation is that the user will have to compute the uncertainty based on his own understanding of the relationships.

5 Homogeneity of materials

Most RMs are subjected to a preparation procedure which ultimately includes subdivision into usable units. A subset of individual units from the batch is chosen for measurement according to a statistically valid sampling plan. A measurement uncertainty is derived taking into account material inhomogeneity as well as other factors (see clause 4). Other types of RM are prepared as individual artifacts and the certification is based on separate measurement of each unit rather than on statistical sampling of the complete batch. The second approach is useful when the RM can be measured non-destructively.

5.1 Materials

RMs prepared as solutions or pure compounds are expected to be homogeneous on physical (thermodynamic) grounds. The object of the test for homogeneity is mainly to detect any impurities, interferences or irregularities.

Materials such as mixed powders, ores, alloys, etc. are heterogeneous in composition by nature. RMs prepared from such materials must therefore be tested to assess the degree of homogeneity.

5.2 Concept of homogeneity

In theory, a material is perfectly homogeneous with respect to a given characteristic if there is no difference between the value of this characteristic from one part (unit) to another. However, in practice a material is accepted to be homogeneous with respect to a given characteristic if a difference between the value of this characteristic from one part (or unit) to another cannot be detected experimentally. The practical concept of homogeneity therefore embodies both a specificity to the characteristic and a parameter of measurement (usually the standard deviation) of the measurement method used, including the defined sample size of the test portion.

5.2.1 Characteristic of interest

A material may be sufficiently homogeneous with respect to the characteristic of interest to be useful as an RM even though it is inhomogeneous with respect to other characteristics, provided that this inhomogeneity exerts no detectable influence on the accuracy and precision of the commonly used methods of determination for the characteristic of interest.

5.2.2 Homogeneity measurement method

The degree of homogeneity that a material must have for use as an RM is commensurate with the precision attainable by the best available methods for the determination of the characteristic for which the RM is intended. Therefore, the greater the precision of the measurement method, the higher is the required degree of homogeneity of the material.

The precision attainable by the homogeneity measurement method varies with both the characteristic measured and its value for the RM. An RM intended for more than one characteristic is described by a corresponding number of statements of homogeneity, each of which should be traceable to an experimentally determined precision. The magnitude of the precision can vary widely.

In many cases, the precision attainable by a measurement method is affected by the size of the test portion taken from the RM. The degree of homogeneity of an RM is therefore defined for a given test portion size.

5.2.3 Practice

Ideally, an RM should be characterized with respect to the degree of homogeneity for each characteristic of interest. For RMs intended for a relatively large number of characteristics, the assessment of the degree of homogeneity for all characteristics is both economically and physically burdensome, and in some cases unfeasible. In practice therefore, the degree of homogeneity of such RMs is assessed only for selected characteristics. It is recommended that these characteristics be appropriately selected on the basis of established chemical or physical relationships; for example, an interelement concomitance in the mineral phases of an RM makes reasonable the assumption that the RM also has an acceptable degree of homogeneity for the non-selected elements.

5.3 Experimental design

5.3.1 Objectives

For reference materials that are expected to be homogeneous on physical grounds, the main purpose of homogeneity testing is to detect unexpected problems. Some examples are differential contamination during the final packaging into individual units, or incomplete dissolution or equilibration of an analyte in a solvent (which could lead to steadily changing concentrations from the first vial filled to the last). A statistical trend analysis would be helpful in the latter case. If the material is produced in more than one batch, it is necessary to test the equality of the batches (or to certify the batches separately).

When the nature of a reference material leads one to expect some inhomogeneity, the goal of the testing programme is not simply detection of inhomogeneity, but rather the estimation of its magnitude. This may require a more extensive testing programme than is required for detection.

Inhomogeneity can manifest itself in at least two ways :

a) different subsamples of an RM unit may differ on the property of interest;

b) there may be differences between units of the RM.

Differences among subsamples can usually be reduced or controlled to an acceptably-low level by making the size of the subsample sufficiently large. Often a study to determine the appropriate subsample size is conducted before the certification experiments are begun. Differences which exist between individual units of the candidate RM must be reflected in the uncertainty statement on the certificate.

In statistical terms, the experimental design must satisfy the following objectives :

1) to detect whether the within-unit (short-range) variation is statistically significant in comparison with the known variation of the measurement method;

2) to detect whether the between-units (long-range) variation is statistically significant in comparison with the within-unit variation;

3) to conclude whether a detected statistical significance for one or both of the within-unit and between-units variations indicates a corresponding physical significance of sufficient magnitude to disqualify the candidate RM for the intended use.

The degree of homogeneity of a candidate RM in final form should be known. The task for the assessment of the homogeneity can, however, be performed in several steps.

5.3.2 Preliminary test for homogeneity

A preliminary assessment of the homogeneity of a candidate RM can be performed after homogenization as an integral part of the preparation process. The physical properties of an RM that can cause segregation to occur, for example the type of blender, strongly influence the manner of sample selection. The samples should be taken at regions where physical differences are expected to occur. Random sampling should be adopted only when causes of physical differences are unknown or believed to be absent.

The number of samples taken and replicate determinations thereon should be such that the appropriate statistical test should be capable of detecting the possible existence of inhomogeneity at a predetermined level.

NOTE – ASTM E 826-81, *Standard practice for testing homogeneity of materials for the development of reference materials*, gives one detailed procedure for testing homogeneity of bulk material. This standard practice is specialized to the case of testing the homogeneity of metals, in either solid or powdered form, and finely ground oxide materials that are intended for use as reference materials in X-ray emission, or optical emission spectroscopy, or both. For most RM certification programmes, an appropriate preliminary test for homogeneity can be obtained by straightforward adaptation of the practice given in ASTM E 826-81.

5.3.3 Principal test for homogeneity

This test must be performed for the candidate RM after it has been packaged into final form regardless of whether a preliminary test for homogeneity has been done. The purpose of the test is to confirm that the between-units variation is not statistically and practically significant.

The units should be selected from the stock at random to give each unit an equal chance for selection. An experimental design should be used in which k units of material are selected and n replicate determinations are performed for each unit. It is recommended that the determinations be performed in random order to avoid possible systematic time variations. k and n should be sufficiently large to detect the possible existence of inhomogeneity at a predetermined level.

For certain RMs, replicate within-unit determinations are not possible because the use of the entire unit is prescribed by the producer. In this instance, the between-units variance must be compared with the estimated precision of the measurement method to assess the degree of homogeneity of the RM.

5.4 Possible outcomes of homogeneity testing

The selection of samples and the analysis of data are usually performed in consultation with a statistician. Depending on the form of material, the emphasis may be to detect trends or patterns, for example from one end to the other of a steel rod, from the centre to the edge of a plate, from the top to the bottom portion of bulk material in a drum; or to check on the variability of material among ampoules or bottles. A proper, statistically designed experiment helps to assure that conclusions are valid, and minimizes the number of measurements needed to reach such conclusions.

The possible outcomes of homogeneity testing are described in 5.4.1 to 5.4.3.

5.4.1 Very homogeneous material

Homogeneity is not a problem, or material variability is negligible in relation to either measurement errors or to the use of the CRM. In this case, the certified value is the best estimate of the mean property value for the lot and the allowance for uncertainty describes possible measurement error associated with that estimate.

5.4.2 Very inhomogeneous material

Material variability is a major factor in the total uncertainty. In this case the entire lot of material is rejected or reworked, or each specimen is individually measured and certified.

Reworking is a reasonable course of action when there is reason to believe that the source of inhomogeneity can be eliminated by preparing a new batch of material using improved procedures. However, this is not always possible, and it is sometimes necessary to tolerate a small amount of between-units inhomogeneity when the material cannot practically be improved.

5.4.3 Material of moderate homogeneity

Material variability is of the same magnitude as the measurement error, and must be included as a component of the uncertainty. This case is discussed in 5.5.

5.5 Some examples of homogeneity testing

Of the three cases (5.4.1 to 5.4.3) the last is the one most frequently encountered. Two subclasses are apparent : one where a trend is detected and one where no trend is detected.

Where a trend has been detected, for example along a steel rod to be cut into pieces, the unusable portion is discarded and, hopefully, the trend in the remaining portion is linear or can otherwise be described mathematically. In such cases, a line (or other appropriate mathematical expression) can be fitted to the values measured along the rod. The maximum departure from the average points on the fitted line is taken as a measure of inhomogeneity, assuming measurement error is small in comparison to the trend.

Where no trend is detected, but the results of measurements show variability that is not negligible, a statistical concept called

"statistical tolerance interval" can be used. To illustrate this concept, suppose a solution is prepared and packaged into 1 000 ampoules, of which 30 are measured for some property. For this example, the tolerance limit concept[1][8] states essentially that based on the measured values of the 30 ampoules almost all of the 1 000 ampoules will not differ from the average of the 30 ampoules by more than the constructed limit. In statistical terms, it would read: "The tolerance interval (mean $\pm$ Δ) is constructed such that it will cover at least 95 % of the population with probability 0,99". [1)]

This statement does not guarantee that the tolerance interval will include all of the ampoules. It says that 99 % of the time the tolerance interval will include at least 95 % of the ampoules. The "99 % of the time" refers to the way this tolerance interval is constructed, i.e., if 30 ampoules were selected from the population repeatedly, and the same experiments were performed over and over again, 99 % of the tolerance intervals so constructed would cover at least the proportion (95 %) of the total population as specified, and 1 % of the tolerance intervals would cover less than 95 % of the total population.

How is this interval constructed ? First, the mean [equation (3)] and standard deviation [equation (4)] from the 30 ampoules are computed :

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i \qquad \ldots (3)$$

$$s = \left[\frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2 \right]^{1/2} \qquad \ldots (4)$$

where

$x_1, x_2, \ldots, x_i, \ldots, x_n$ are the measured values, with $n = 30$;

$\bar{x}$ is an estimate of the mean, μ, of the 1 000 ampoules;

s is an estimate of the measure of the dispersion, σ, among these ampoules.

The values $\bar{x}$ and s contain practically all the information available on the 1 000 ampoules and can be used to calculate the tolerance interval $\bar{x} \pm \Delta$.

The value of Δ is computed as a multiple of s, i.e. $\Delta = k'_2 s$. The value of k'_2 depends on three parameters :

a) the number, n, of samples measured (30);

b) the proportion, p, of the total population to be covered (0,95);

c) the probability level, $1 - \alpha$, specified (0,99).

A table of factors for two-sided tolerance limits for normal distributions gives the value for k'_2 as 2,841 for $n = 30$; $1 - \alpha = 0{,}99$; and $p = 0{,}95$. Tables of these factors are given in ISO 3207 [2)] and in many standard statistical texts[1][8].

The term "two-sided" means that we are interested in both over and under limits from the average. The term "normal distribution" refers to the distribution of all the values of interest and is a symmetrical, bell-shaped distribution usually encountered in precision measurement work.

Figure 2 is a histogram of the ratios of the emission rate of ^{137}Cs, in a ^{137}Cs nuclear fuel burn-up reference material, to a radium reference standard. A frequency curve of a normal distribution can be fitted to these data. There were 98 ampoules of ^{137}Cs involved; each ampoule was measured in April, September, and November, 1972. By averaging the three measurements, the measurement error was considerably smaller than the difference of masses of active solutions among these ampoules, and the plot in figure 2 shows essentially the inhomogeneity of the mass of solution in the ampoules.

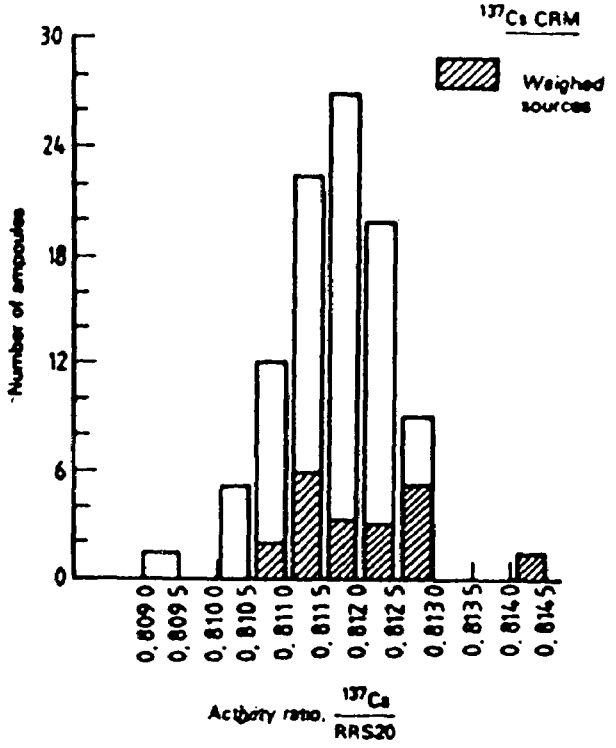


Figure 2 – Histogram of the frequency (number of ampoules) versus the ratio of the activity of ^{137}Cs standards to a radium reference standard (RRS20)

1) The statement is true only for a population of infinite size; however, the correction for a population of finite size is negligible where finite size is large.

2) ISO 3207, *Statistical interpretation of data – Determination of a statistical tolerance interval.*

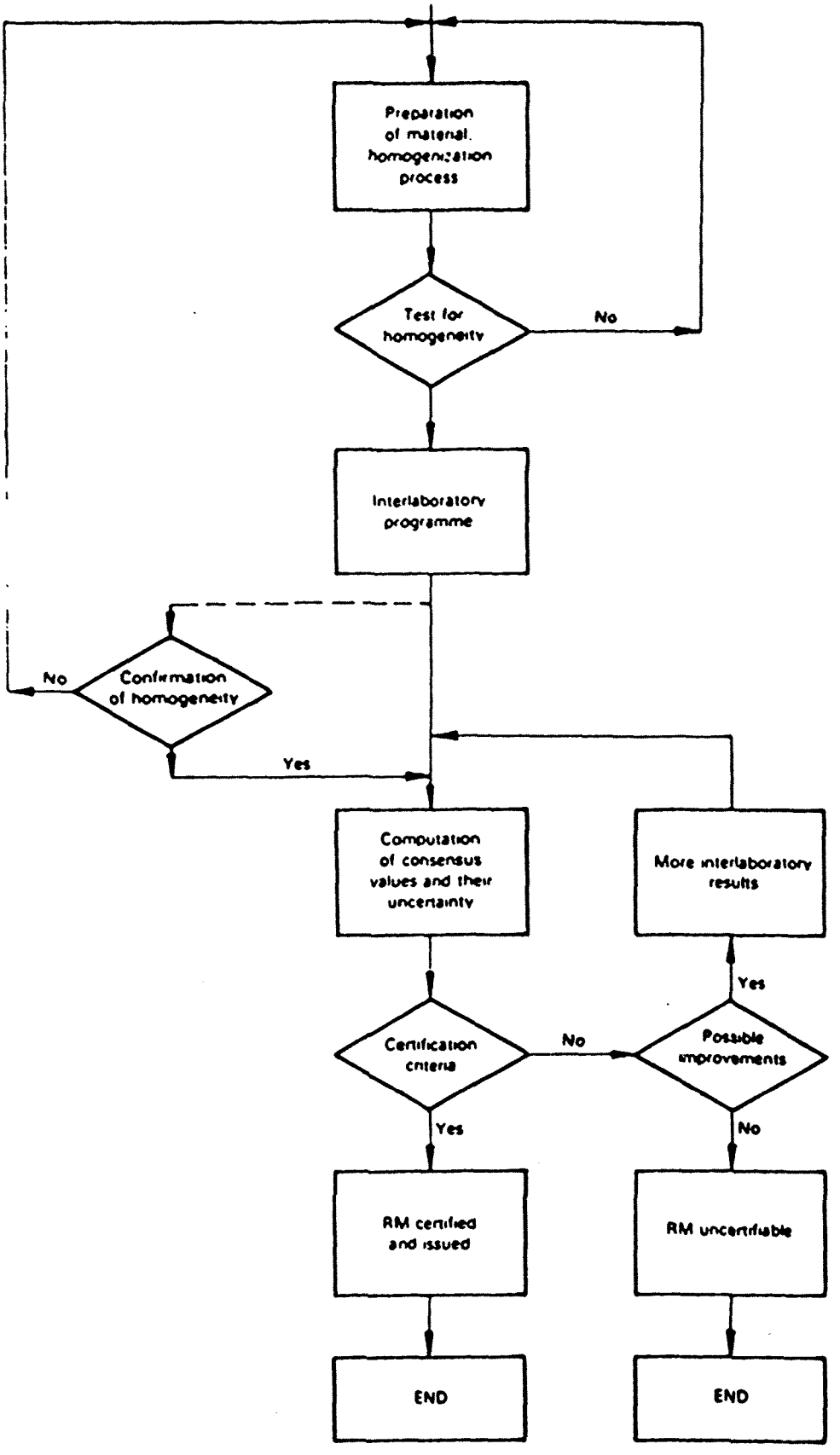


Figure 3 – Schematic diagram of the process of preparation and certification of an RM by interlaboratory consensus

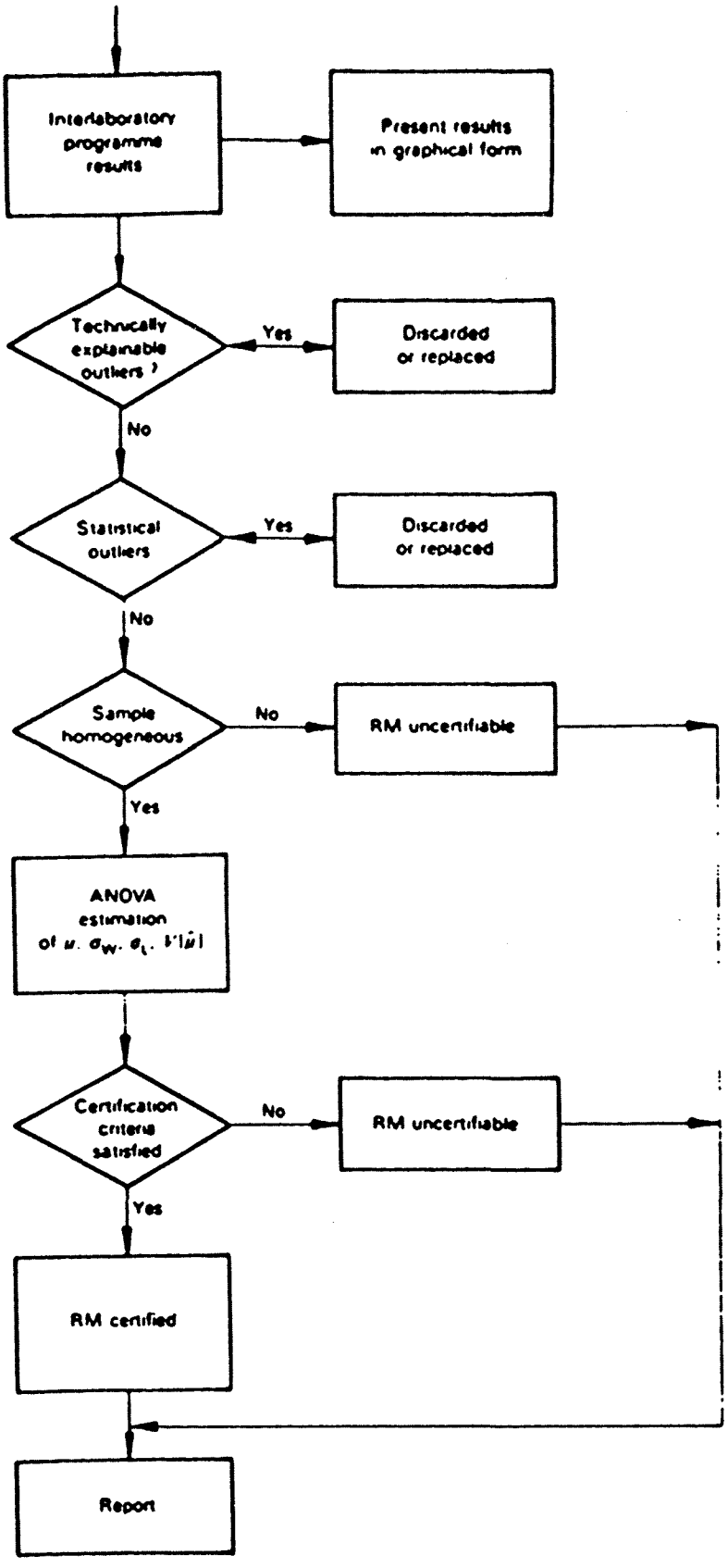


Figure 4 — Schematic diagram for statistical evaluation of interlaboratory results

8.3.6 Statistical outliers

A single result or an entire set of results is suspected to be a statistical outlier if its deviation either in accuracy or precision from others in the set or other sets, respectively, is greater than can be justified by statistical fluctuations pertinent to a given frequency distribution. Therefore, the effectiveness for the detection of outliers depends on the validity of the assumption of the frequency distribution. The test for outliers should be the statistician's prerogative. For an interlaboratory programme outlying status may be conferred on individual results, results for individual units or the entire set of results from a laboratory.

8.4 Statistical analysis

8.4.1 Two-stage nested design

This model is used when the results of an interlaboratory programme are used to confirm the homogeneity as well as to characterize the material. The experimental scheme is illustrated schematically in figure 5 a). The results can be expressed by the equation

$$X_{ijk} = \mu + a_i + \beta_{ij} + \varepsilon_{ijk} \qquad \ldots (5)$$

where

X_{ijk} is the kth result of sample unit j reported by laboratory i;

μ is the grand mean;

a_i is the error due to laboratory i;

β_{ij} is the error due to the jth sample unit in laboratory i;

ε_{ijk} is the measurement error.

8.4.2 One-stage nested design

This model is used when the material is accepted to be homogeneous by the organizers. The experimental scheme is illustrated schematically in figure 5 b). Equation (5) can then be simplified to

$$X_{ik} = \mu + a_i + \varepsilon_{ik}$$

8.4.3 Analysis of two-stage nested design

Parameters to be estimated are

— μ, the grand mean (which is used as the consensus value);

— σ_L^2, the variance of the between-laboratories error (a_i);

— σ_U^2, the variance due to between-units inhomogeneity (β_{ij});

— σ_W^2, the variance of the within-laboratory measurement error (ε_{ijk}).

All these parameters can be estimated simultaneously by the analysis of variance (ANOVA) method (see 8.4.3.1) if there are sufficient results of equal replication (the same number of replicate determinations from each unit and the same number of units per laboratory) after outliers have been excluded. If this ANOVA requirement cannot be met because of the number of outliers and/or missing results, the significance of the between-units (inhomogeneity) variance can be tested by the simple procedure for unbalanced data given in 8.4.3.2.

Theoretical details and additional methods for balanced and unbalanced ANOVA are given in standard textbooks. [27, 28]

8.4.3.1 Computation of two-stage ANOVA

x_{ijk} is the kth result of sample unit j reported by laboratory i;

p is the number of participating laboratories;

q is the number of units per laboratory;

n is the number of replicate determinations per sample unit.

$$\bar{x}_{ij} = \frac{1}{n} \sum_{k=1}^{n} x_{ijk}$$

$$\bar{x}_i = \frac{1}{q} \sum_{j=1}^{q} \bar{x}_{ij}$$

$$\bar{x} = \frac{1}{p} \sum_{i=1}^{p} \bar{x}_i$$

The sums of the squares SS_1, SS_2 and SS_3 are calculated by the following equations :

$$SS_1 = qn \sum_{i=1}^{p} (\bar{x}_i - \bar{x})^2$$

$$SS_2 = n \sum_{i=1}^{p} \sum_{j=1}^{q} (\bar{x}_{ij} - \bar{x}_i)^2$$

$$SS_3 = \sum_{i=1}^{p} \sum_{j=1}^{q} \sum_{k=1}^{n} (x_{ijk} - \bar{x}_{ij})^2$$

The degrees of freedom are

$$f_1 = p - 1$$

$$f_2 = p(q - 1)$$

$$f_3 = pq(n - 1)$$

and each mean square is given as

$$MS_1 = SS_1/f_1$$

$$MS_2 = SS_2/f_2$$

$$MS_3 = SS_3/f_3$$

These results should be tabulated (see table 1).

Table 1 – ANOVA table

Source	Sum of squares	Degrees of freedom	Mean square	Expectation of mean square
Between laboratories	SS_1	$p - 1$	MS_1	$\sigma_W^2 + n\sigma_U^2 + qn\sigma_L^2$
Between units	SS_2	$p(q - 1)$	MS_2	$\sigma_W^2 + n\sigma_U^2$
Measurement error	SS_3	$pq(n - 1)$	MS_3	σ_W^2

Each parameter is estimated by the following equations, where the circumflex denotes the estimate :

$$\hat{\mu} = \bar{\bar{x}}$$

$$\hat{\sigma}_L^2 = (MS_1 - MS_2)/qn$$

$$\hat{\sigma}_U^2 = (MS_2 - MS_3)/n$$

$$\hat{\sigma}_W^2 = MS_3$$

If the numerical value of $\hat{\sigma}_L^2$ or $\hat{\sigma}_U^2$ is negative, zero should be used instead.

The tests for statistical significance are

a) between-units (inhomogeneity) variance

$$F_{2|3} = MS_2/MS_3$$

which should be compared with the critical value of the F-distribution for degrees of freedom $p(q - 1)$ and $pq(n - 1)$;

b) between-laboratories variance

$$F_{1|2} = MS_1/MS_2$$

which should be compared with the critical value of the F-distribution for degrees of freedom $(p - 1)$ and $p(q - 1)$.

The variance of the consensus value $\bar{\bar{x}}$ is estimated by

$$\hat{V}(\bar{\bar{x}}) = \frac{MS_1}{pqn}$$

The confidence interval for μ based on $\bar{\bar{x}}$ is from A to B where

$$A = \bar{\bar{x}} - t_{1-\alpha/2}(p - 1)\sqrt{\frac{MS_1}{pqn}}$$

$$B = \bar{\bar{x}} + t_{1-\alpha/2}(p - 1)\sqrt{\frac{MS_1}{pqn}}$$

where $t_{1-\alpha/2}(p - 1)$ is the $1 - \alpha/2$ fractile of the t-distribution with $(p - 1)$ degrees of freedom.

8.4.3.2 Modified ANOVA for unbalanced data

x_{ijk} is the kth result of sample unit j reported by laboratory i;

p is the number of participating laboratories

q_i is the number of units at laboratory i;

n_{ij} is the number of replicate determinations of sample unit ij.

$$\bar{x}_{ij} = \frac{1}{n_{ij}} \sum_{k=1}^{n_{ij}} x_{ijk}$$

$$\bar{x}_i = \frac{\sum_{j=1}^{q_i} n_{ij}\bar{x}_{ij}}{\sum_{j=1}^{q_i} n_{ij}}$$

The sums of the squares SS_2 and SS_3 are calculated by the following equations :

$$SS_2 = \sum_{i=1}^{p}\sum_{j=1}^{q_i} n_{ij}(\bar{x}_{ij} - \bar{x}_i)^2$$

$$SS_3 = \sum_{i=1}^{p}\sum_{j=1}^{q_i}\sum_{k=1}^{n_{ij}} (x_{ijk} - \bar{x}_{ij})^2$$

The degrees of freedom are

$$f_2 = \sum_{i=1}^{p} (q_i - 1)$$

$$f_3 = \sum_{i=1}^{p}\sum_{j=1}^{q_i} (n_{ij} - 1)$$

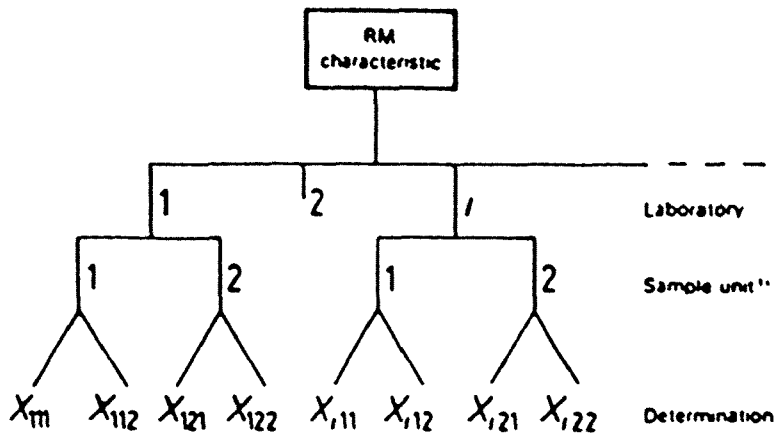
and the mean squares are given as

$$MS_2 = SS_2/f_2$$

$$MS_3 = SS_3/f_3$$

These results should be tabulated (see table 2).

a) Two-stage nested design



1) All sample units are different. However, in each laboratory they are numbered 1, 2.

b) One-stage nested design

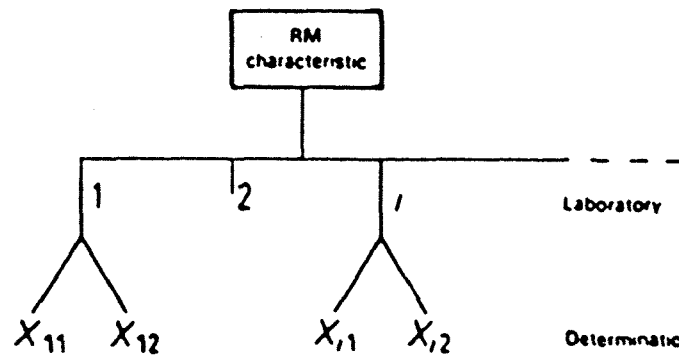


Figure 5 — Experimental scheme for an interlaboratory programme

Table 2 – ANOVA table

Source	Sum of squares	Degrees of freedom	Mean square
Between units	SS_2	f_2	MS_2
Measurement error	SS_3	f_3	MS_3

The test for statistical significance of the between-units (inhomogeneity) variance is

$$F_{2|3} = MS_2/MS_3$$

which should be compared with the critical value of the F-distribution for degrees of freedom

$\left\{\sum_i (q_i - 1)\right\}$ and $\left\{\sum_i \sum_j (n_{ij} - 1)\right\}$.

8.4.4 Analysis of one-stage nested design

For cases where the material is considered to be homogeneous, i.e. that all units are identical, all results reported by a laboratory are considered as replicates.

x_{ij} is the jth result reported by laboratory i;

p is the number of participating laboratories;

n_i is the number of results reported by laboratory i.

$$\bar{x}_i = \frac{1}{n_i} \sum_{j=1}^{n_i} x_{ij}$$

$$\bar{\bar{x}} = \frac{1}{p} \sum_{i=1}^{p} \bar{x}_i$$

The variance of the consensus value, $\bar{\bar{x}}$ is simply estimated by

$$\hat{V}(\bar{\bar{x}}) = \frac{1}{p(p-1)} \sum_{i=1}^{p} (\bar{x}_i - \bar{\bar{x}})^2$$

with degrees of freedom $(p - 1)$.

The confidence interval for the consensus value (mean of means) is the interval from A to B where

$$A = \bar{\bar{x}} - t_{1-\alpha/2}(p-1)\left(\hat{V}(\bar{\bar{x}})\right)^{1/2}$$

$$B = \bar{\bar{x}} + t_{1-\alpha/2}(p-1)\left(\hat{V}(\bar{\bar{x}})\right)^{1/2}$$

and $t_{1-\alpha/2}(p - 1)$ is as described in 8.4.3.1.

9 Certification based on a metrological approach

9.1 Concepts

The objective of this approach is to produce certified values the accuracy and the uncertainty of which are demonstrated by experimental evidence.

The first basic concept behind this approach is that when the property, physical or chemical, of a material can be defined from first principles, its value does not depend on a particular method used for the measurement.[1] When the value of such a property is to be certified, it is therefore important for the certification body to show that the value does not include a systematic error specific to a method or to a laboratory. The procedure consists in measuring the property under consideration by different methods which are considered to be the most accurate in the actual state of the art and applied by laboratories most experienced for the respective methods. This approach is also adopted by establishments working alone : they use several methods, possibly with operators working independently, and compare the results.

The second concept is that the uncertainty statement, which is an important part of the value assigned to a measurement standard, can fail to be reliable when it is not based on a very careful comparison between results of different (high level) laboratories and different methods. This is illustrated by examples in 9.2 and 9.3.

The measurement of the quantities referred to above is traceable or should be traceable to measurement scales, themselves traceable to the SI. By definition, the traceability is the property of a result of a measurement whereby it can be related to appropriate standards through an unbroken chain of comparisons.

The traceability is necessary to support the concept of accuracy. The traceability of analytical processes is more difficult to establish than in physical measurements. The problems involved in this traceability are discussed in detail in 9.3.

In 9.4, examples are given of properties which are defined only by a method and can be traceable only to a conventional measurement scale.

9.2 Certification of physical properties

The most accurate measurements are carried out for fundamental units, their most common multiples and their submultiples, in the primary metrology laboratories. Here, all sources of errors and uncertainties are investigated in great detail; methods of measurement have been improved over many years to reduce uncertainties. The accuracy of these measurements is fairly well established, especially when they have been the subject of interlaboratory comparisons. Reservations must be made for measurements where there has been no intercomparison. In addition, any new laboratory being established needs extensive intercomparisons to ensure that its

1) There are properties which are defined only as a function of a method; this question is examined in 9.4.

own estimates of accuracy are correct and that no error has escaped its attention.

Intercomparisons add confidence to the uncertainty computed by the metrology laboratories individually. Sometimes they use safety factors which are not necessary; sometimes they underestimate their own uncertainties.

The present practice by which each metrology laboratory evaluates the uncertainty of a particular measurement on its own is inherently dangerous. It is not possible for a laboratory alone to avoid all errors in all circumstances, in particular for derived units. Intercomparisons detect errors that were not taken into account and situations where all parameters influencing the measurements are not sufficiently well controlled.

There is unfortunately no general requirement in metrology that uncertainty statements be based on appropriate intercomparisons. Certifying a reference material on the basis of results of one single metrology laboratory may therefore imply a risk which should not be overlooked.

When the certification of a physical property or quantity is undertaken, it is therefore important to have an intercomparison between the major metrology laboratories followed by a full discussion of the results with all participants to resolve any possible discrepancy. If the primary metrology laboratories are not themselves involved in the measurement, complete traceability of the participating laboratories to the respective national laboratories must be established before starting.

The participants must then compare their measurements and discuss all the possible errors responsible for discrepancies and eliminate them while remaining independent. This is described in more detail for chemical measurements in 9.3.2.

If more than one method is possible, and if these methods appear equally valid, it is important to compare them. However, it is useful to remember that the method with the shortest traceability route or, in other words, with the most direct connection to the fundamental units, has a higher probability of being more accurate.

At the limit, there can of course exist situations where one single laboratory, having compared its method with all possible others and having eliminated most causes of errors, is able to refine its method to reduce the uncertainty while taking considerable precautions to avoid any accidental source of errors.

Some measurement problems in the field of physical properties can be briefly illustrated by thermal conductivity of insulation and refractory materials. Until some years ago, laboratories were not able to carry out such measurements with appropriate accuracy although the calibration of the instrumentation appeared satisfactory. The guarded hot-plate used for the measurement was constructed and operated in accordance with existing national and international standards. The agreement appeared satisfactory for simple technical applications. However, in most laboratories there was a systematic error. Heat losses occurred above room temperature because the guard ring was not sufficient. Any reference material certified on that basis would have a wrong traceability. The method and equipment were therefore modified until the heat losses became negligible.

The accurate determination of thermal conductivity of refractory materials is very difficult by the direct method using the guarded hot-plate apparatus mainly because of the heat losses and experimental difficulties. Methods such as the hot-wire method or the flash method do not present such difficulties, but their traceability is not easy to establish and therefore these methods are not the best for certification. However, the results of these methods are important as a verification of the results of the guarded hot-plate.

9.3 Certification of a chemical composition

9.3.1 Traceability

In the field of analytical chemistry, there is no established measurement system organized as in the field of metrology, with primary and calibration laboratories, and measurement standards available for circulation. The concept of accuracy is hence more difficult to reach and the traceability is more difficult to realize.

In chemistry, the calibrations in the usual sense are not the major source of difficulties although the task of the chemist is heavier than that of the metrologist. He needs not only physical standards of mass, volume, temperature, etc., but also standards of all chemical species he has to determine : elements, organic compounds, etc. Each one of these chemical standards has an uncertainty (e.g. impurities) which is sometimes underestimated.

The biggest problem is however the traceability of the overall analytical process : the traceability chain is broken every time the sample is physically or chemically modified in the analytical process.

As the variety of sample processing procedures is large, it is not possible to discuss the traceability in general. The following paragraphs are to be considered only as examples.

9.3.1.1 Sample weighing

The first step of the analytical process is the weighing of the sample. This does not pose problems of traceability if the balance is periodically calibrated. Human errors are not excluded but they are not frequent.

9.3.1.2 Sample treatment

Whenever the sample is dissolved or submitted to similar treatment, the traceability chain is broken and any uncertainty evaluation should take this into account. To establish traceability for that part of the measurement procedure, a laboratory must demonstrate the relationship between the initial sample and the solution prepared from it. The main questions to be answered are, was the sample totally dissolved, what were the losses, were there contaminations? If the analysis is to determine not one element but a compound, was the compound changed during the dissolution step? In the case of organic compounds, the efficiency of extraction is one of the main causes of difficulties.

Table 3 — Trace elements in milk

Values in nanograms per gram

Element	First intercomparison (range of results)	Certification campaign (range of results)	Certified
Cd	0,4 to 4 500	1 to 5,6	2,9
Hg	0,6 to 42	0,73 to 1,27	1,0
Pb	68 to 5 500	92,4 to 112,5	104,5
Cu	470 to 9 257	475 to 700	545

Table 4 — Results of analyses of olive-tree leaves

Element	1978 results µg/g	Ratio	1981 results µg/g	Ratio
Cd	0,050 to 6,654	133	0,054 3 to 0,121	2,2
Pb	17,6 to 33,3	1,9	20,2 to 26,4	1,3
Hg	0,005 to 0,702	140	0,247 to 0,336	1,4
Cu	0,5 to 131,9	264	43,2 to 50,8	1,2
Zn	12,3 to 31,6	2,6	14,5 to 17,7	1,2
Mn	0,4 to 4,6	11,5	51 to 61,8	1,2

Table 5 — Determination of pesticides in powdered milk spiked with certain compounds

Compound	Results mg/kg	Ratio	Quantities added mg/kg
HCH	0,001 to 0,22	220	0,28
α-HCH	0,009 to 0,60	67	0,11
γ-HCH	0,001 14 to 0,18	158	0,20
DDE	0,004 3 to 0,47	109	0,54
*op'*DDT	0,003 to 0,24	80	–
β-HCH	0,01 to 0,13	13	0,08
β-HEPO	0,001 to 0,13	130	0,12
Dieldrin	0,01 to 0,104	10	0,10
*pp'*DDT	0,005 to 0,36	72	–

— solution treatments,

— errors included in the calibration curve,

— matching the calibration to the product to analyse matrix effects, interferences;

— a second round of analyses with the same laboratories but possibly with a material of slightly different composition;

— discussion;

— further rounds of analyses as necessary.

The procedure described often leads to rejecting some method(s) or to abandoning some laboratories which cannot improve their performance. At the end of this long procedure, one has a set of technically consistent results for which one calculates the mean value, and its 95 % confidence interval (adopted as uncertainty). Examples of successive stages are given in figures 6 and 7. Statistics are used for no other purpose than for verifying that the conditions are fulfilled to calculate a 95 % confidence interval.

The statistics for the calculation are the same as shown in ISO Guide 33[29].

When the results are not consistent, one must conclude that the technical work is not terminated and that certification is not possible.

It is to be noted that for trace elements or for the certification of impurity levels, the distribution of results can be log-normal. The confidence interval can be non-symmetrical.

NOTES

1 The method(s) used to certify a reference material are sometimes very different from the methods used in routine practice (e.g. to certify cortisol in serum one has to use GCMS, while in practice the commonly used method is radio-immunoassay). In these cases it is important to verify that the RM is suitable for use with the routine method.

In figure 9, it should be noted that only the GCMS results were intended for certification. The other methods were used to verify the suitability of the RM.

If, after sample treatment, the solution is subject to further manipulations (preconcentration, precipitation, etc.) each step complicates the traceability route and adds new possibilities of losses or contaminations which must be investigated.

It is well known that some of the parameters listed here depend more on the matrix than on the element or compound to be determined.

9.3.1.3 Final determination

The third step in an analytical process is the final determination. Apart from gravimetry, titrimetry, and coulometry, most methods, for example spectrometry and atomic absorption, are indirect. The instrumentation used for these measurements provides a signal which must be correlated with the concentration of the substance of interest in the unknown sample. That correlation is established by means of a calibration curve.

Here there are two groups of problems to consider :

- is any error introduced in producing the calibration curve and what is the accuracy?
- is it correct to use that particular calibration curve?

If we suppose that the calibration can be done by means of solutions, then the most important parameters to take into account are

- the accuracy of the measurements (mass, volume) made for the preparation of the solution;
- the purity of the elements or substances, the stoichiometry of the compounds, etc.;
- the purity of the water or solvent.

Errors due to the calibration curve are not rare even in good laboratories.

However, as pointed out in 9.3.1.4 even larger errors are due to the fact that users sometimes produce calibration curves which are not appropriate to the solutions they have to analyse; these are named matrix effects, interferences, etc.

In metrological terms, this could be expressed as follows : each laboratory produces for itself a measurement scale which is not fully appropriate to the measurements to be made, and each one produces a different measurement scale.

9.3.1.4 Matrix effect

The response of a particular element to a measurement process (e.g. spectrometry, atomic absorption) may depend on the solution (viscosity, conductivity, ionic strength) or on the ions present in it (interferences).

Besides a large number of such cases in inorganic analyses, severe matrix effects are found in clinical chemistry, where some methods designed to analyse a serum can be wrong for aqueous solutions. For such methods the calibration should be done with human serum; if this is not possible, the validity of any other matrix should be demonstrated.

In this respect the term "calibrant" used by biochemists can be misleading. Similarly, in inorganic chemistry, a calibration solution should simulate very closely the solution to be analysed.

9.3.2 Certification work

The task of any laboratory participating in an exercise to certify a new reference material includes the study of the parameters mentioned in 9.3.1. A full study requires the comparison of different methods of sample treatment and different methods of determination. This can, however, be best done collectively in order to have the collaboration of experienced specialists in each method. In addition, for each method there should be more than one laboratory in order to avoid systematic errors due to laboratory effects or operator effects. It can be pointed out that errors (e.g. those due to contaminations) can only be detected by comparison of results from different laboratories.

The need for scrutinizing carefully the results of the different participants can be illustrated by the examples given in tables 3 and 4, which are rather typical of trace element analysis at very low levels. The laboratories often find values which are too high because they all produce some contamination. If one too quickly adopted the mean value of their results, one would have a systematic error by excess, and a reference material totally unreliable from the point of view of traceability. This explains why the procedure proposed to approach accuracy is composed of several steps in which the participants discuss all sources of errors in all parts of the analytical procedure and then try to reduce them. Analyses are then repeated (possibly not on exactly the same samples) and the results are discussed again as many times as necessary to reach sufficient convergence.

The need for several laboratories also exists in the case of so-called "definitive" methods like IDMS. For one particular determination there may be more than one "definitive" method, or several variations of a definitive method; it is of course essential to verify that they provide the same result and this is not necessarily the case. If, after detailed comparison of the results of several laboratories, it is not possible to identify errors, the variation of results (between laboratories) represents the uncertainty of the technique in the current state of the art. Working with one single laboratory would perhaps lead to a smaller spread of results but this would not necessarily represent the real uncertainty.

To summarize, the certification work in accordance with the approach proposed here would include the following steps for a homogeneous and stable material :

- examination, with experienced laboratories, of the most reliable (accurate) methodologies for the analysis of the element or substance in the particular matrix considered;
- a first round of analyses;
- a detailed discussion of the results with all participants to try to discover explanations of the differences; particular attention is given to
  - sample treatment,
  - possible losses, contaminations,

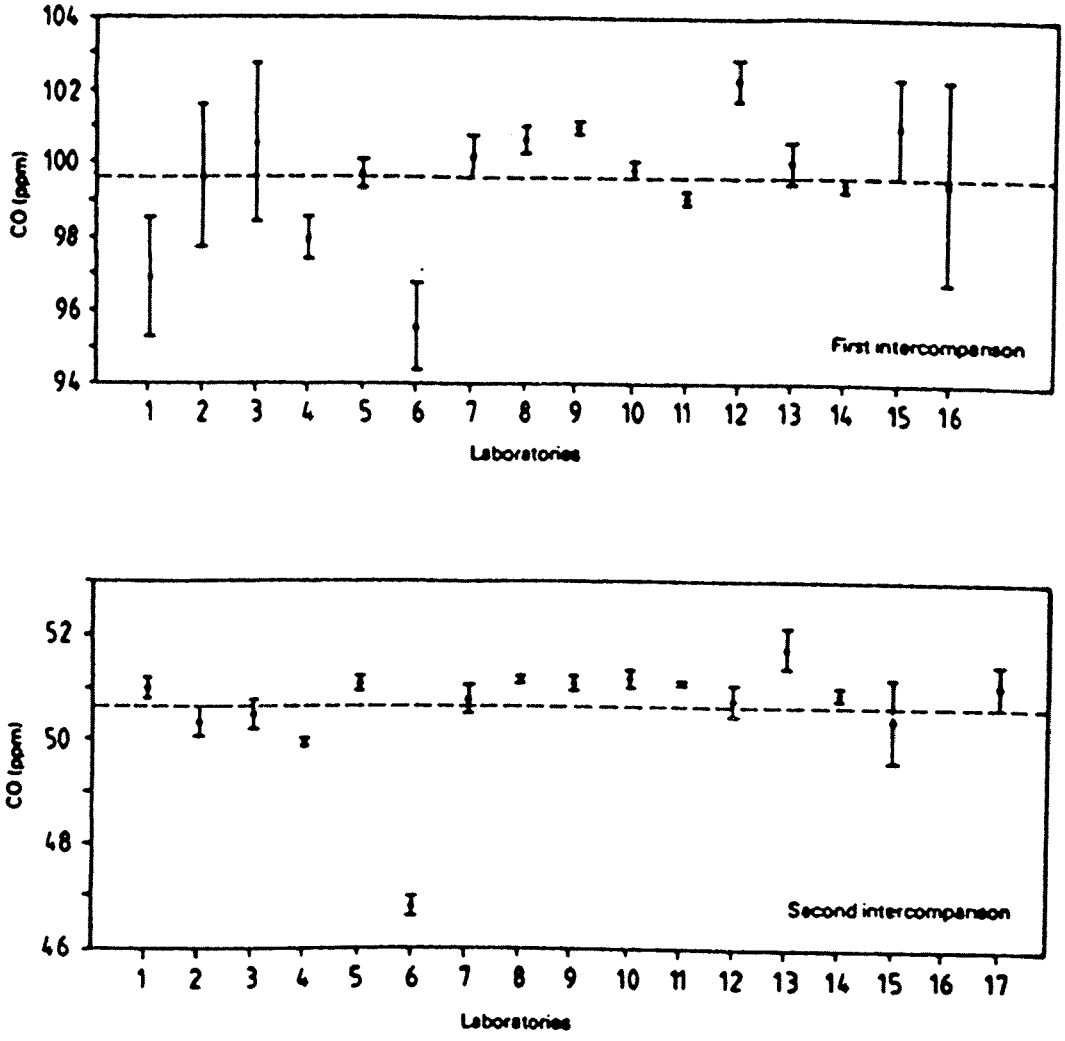


Figure 6 – Results of the first and second intercomparison of analyses of carbon monoxide in nitrogen

2 For the preparation of a reference material in the biomedical field in particular, blood serum is treated with stabilizing agents or is lyophilized. It is then essential to verify the appropriateness of the reference material after these treatments.

9.4 Certification of conventional properties

In chemistry, biochemistry and other technologies, many properties are defined only by a method, a test procedure or particular equipment. Examples are mechanical properties of materials, activity of enzymes, etc. The results of these measurements or tests can be subject to great variability with heavy economic consequences.

As in any other measurement, the results depend on the way in which the procedure is applied. However, the procedure is not always described in all necessary details in the written standards and the operator has no means of verifying if the way he has interpreted and applied the procedure is correct. Hence the need for the reference material.

The diagrams in figure 10 show results of determination of the activity of an enzyme (γ-glutamyltransferase) in an albumin matrix with the same IFCC method. Laboratories shown on the right-hand side had previous training with the method. Laboratories on the left-hand side were high-level scientific laboratories but with no previous experience in the method. While the two upper diagrams in figure 10 relate to one material, the bottom diagram concerns a different material.

Similarly, where a test depends on the use of a particular machine or equipment it is possible, but extremely time-consuming and expensive, to verify that the machine satisfies all specifications. A simple way to by-pass this is to measure or test a reference sample. If the results are satisfactory, it means that the machine is in good condition and that therefore the results can be considered traceable to the measurement scale established by the relevant written standard.

Of course, the certification work to establish reference materials for such properties or measurement scales requires the application of the same principles as explained before. The measurements of these parameters, which may be mass, volume, length or temperature, must themselves be accurate and traceable and therefore may require extensive calibration. Considerable effort is often necessary to investigate the influence of the various parameters of the procedures and of the equipment on the measurement results. The verifications and calibrations must be done independently in a few, if not several, laboratories in order to avoid a uniform bias that would appear as a good agreement and give an illusion of accuracy.

9.5 Use of reference materials for establishing traceability

In 9.3.1, a review was given of a number of parameters that a laboratory should control and verify to ensure the traceability of the determinations. To do this in all necessary details is very hard work.

This can be considerably simplified by the use of a certified reference material of established traceability. The reference material must be sufficiently similar (in matrix) to the actual sample to be analysed in order to include all analytical problems which might cause errors in the determinations. Of course, the user should apply to the reference material the same analytical procedure as for his unknown sample.

When the laboratory using such a reference material finds only a negligible difference with the certification value, this indicates both that the result is accurate and that it is traceable to the fundamental measurement scale. If the difference is not acceptable, it indicates that the measurement procedure includes errors which must be identified and eliminated. It is suggested that the most critical steps subject to errors are the sample treatment and the matching of the calibration.

Hence the role of the reference material is comparable to that of the transfer standards used in metrology laboratories in industry, in that it allows working with a specified margin of uncertainty.

The reference materials also make it possible to establish the uncertainty of a measurement for analytical determinations or technological testing.

The importance of a certified reference material goes therefore beyond the definition of the reference material given in ISO Guide 30[12].

A reference material is used not only

- for calibration of an apparatus,
- for the verification of a measurement procedure,

but also

- for establishing traceability of the measurement results,
- for determining the uncertainty of these results.

Finally, one should not forget that the use of a reference material does not eliminate completely the importance of audits, the purpose of these being to verify that no mistake is made in the use of the RM.

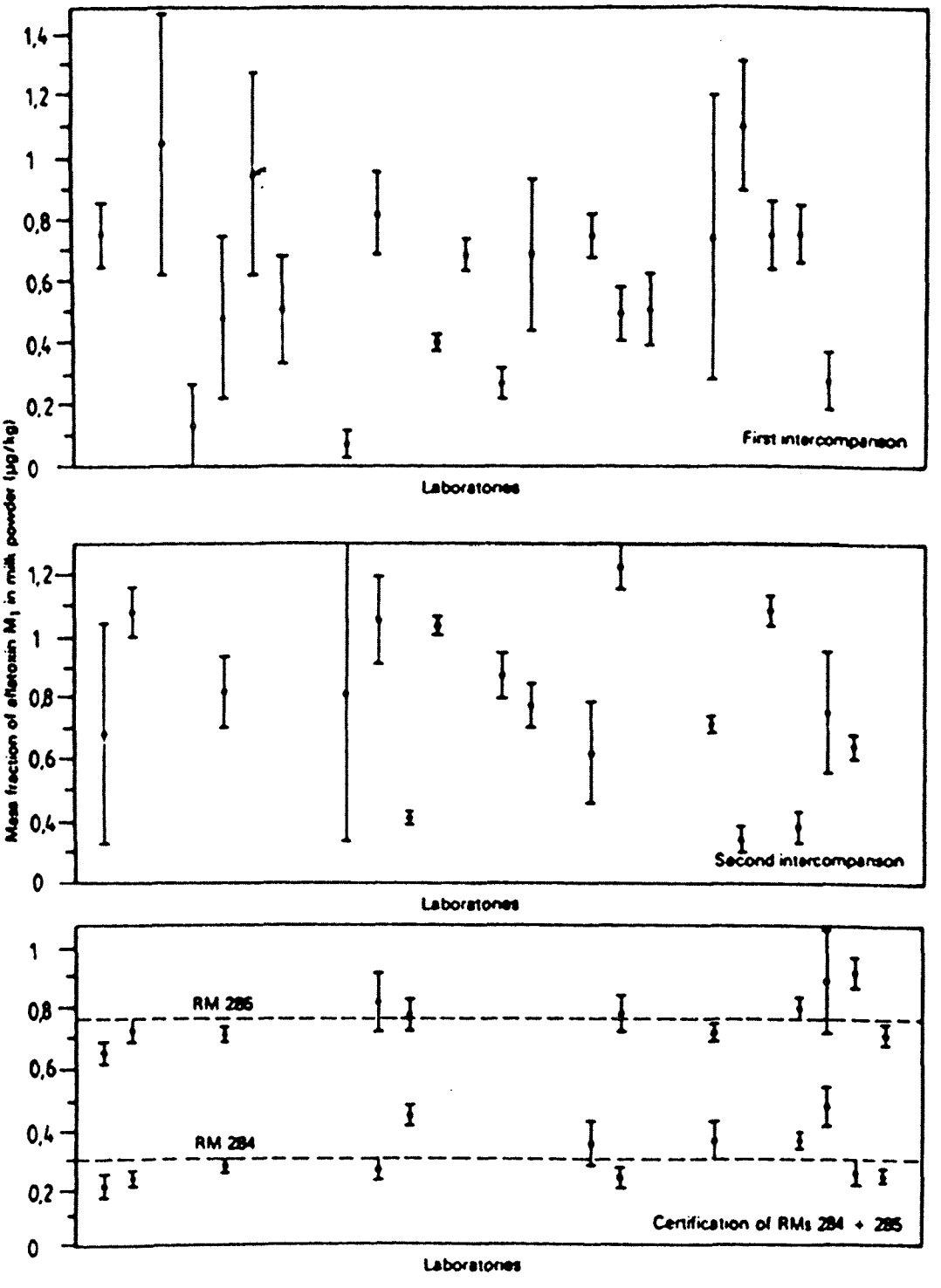


Figure 7 – Evolution of results in successive intercomparisons for the determination of aflatoxin in milk powder

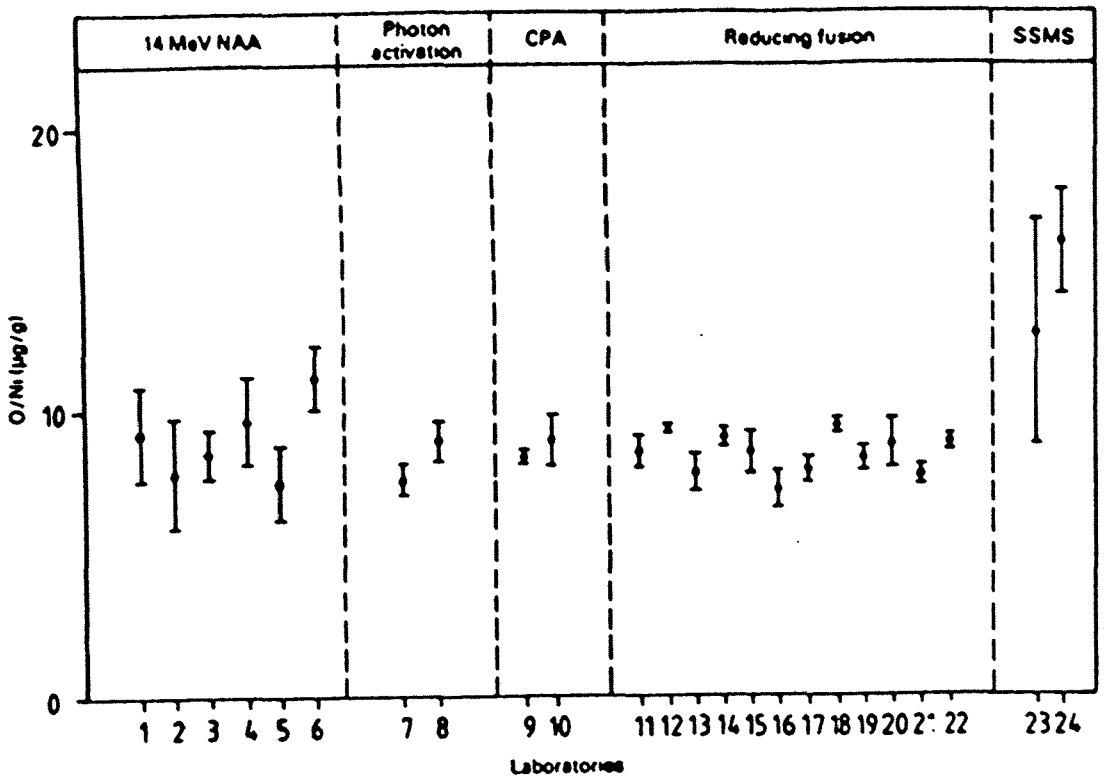
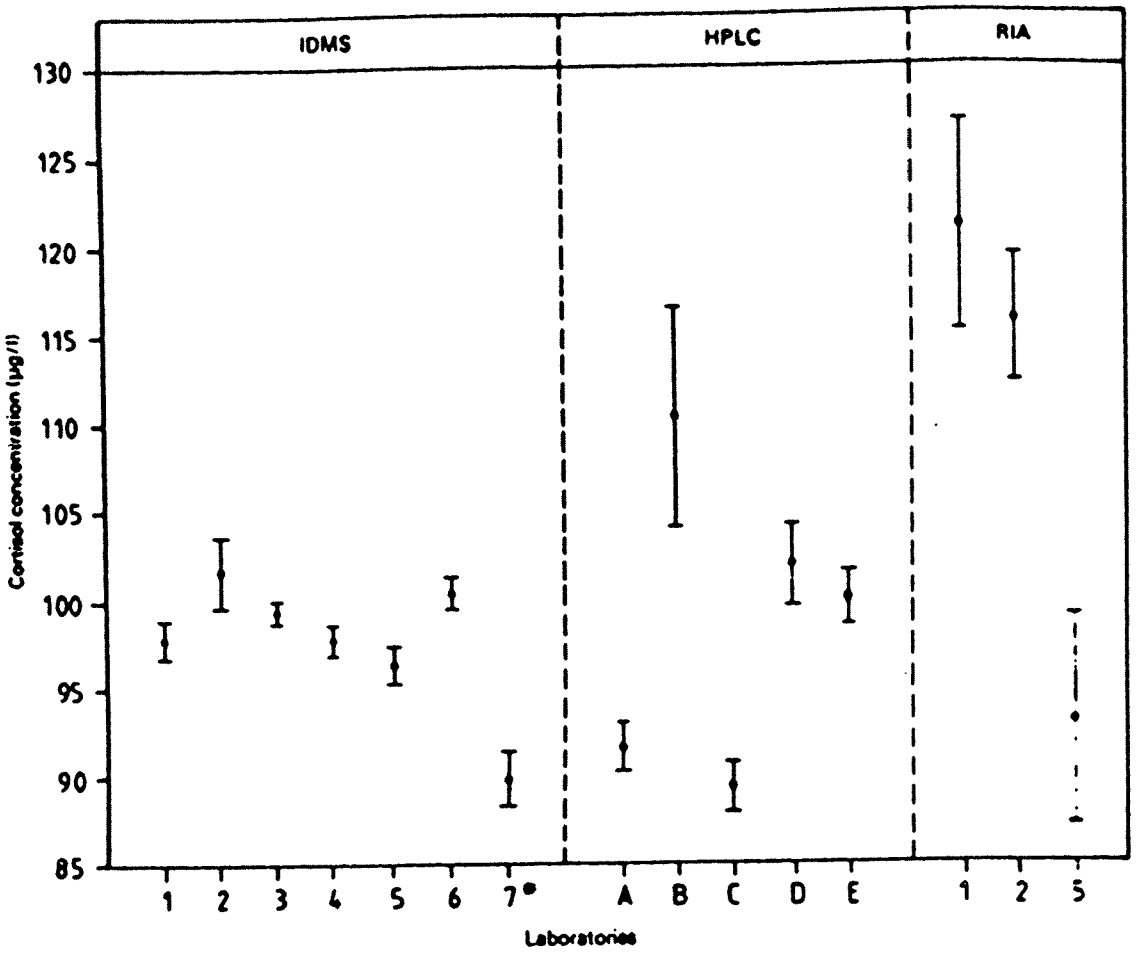


Figure 8 — Results of individual laboratories for oxygen/nickel ratio



* Excluded for certification

Figure 9 – Determination of cortisol in reconstituted human serum

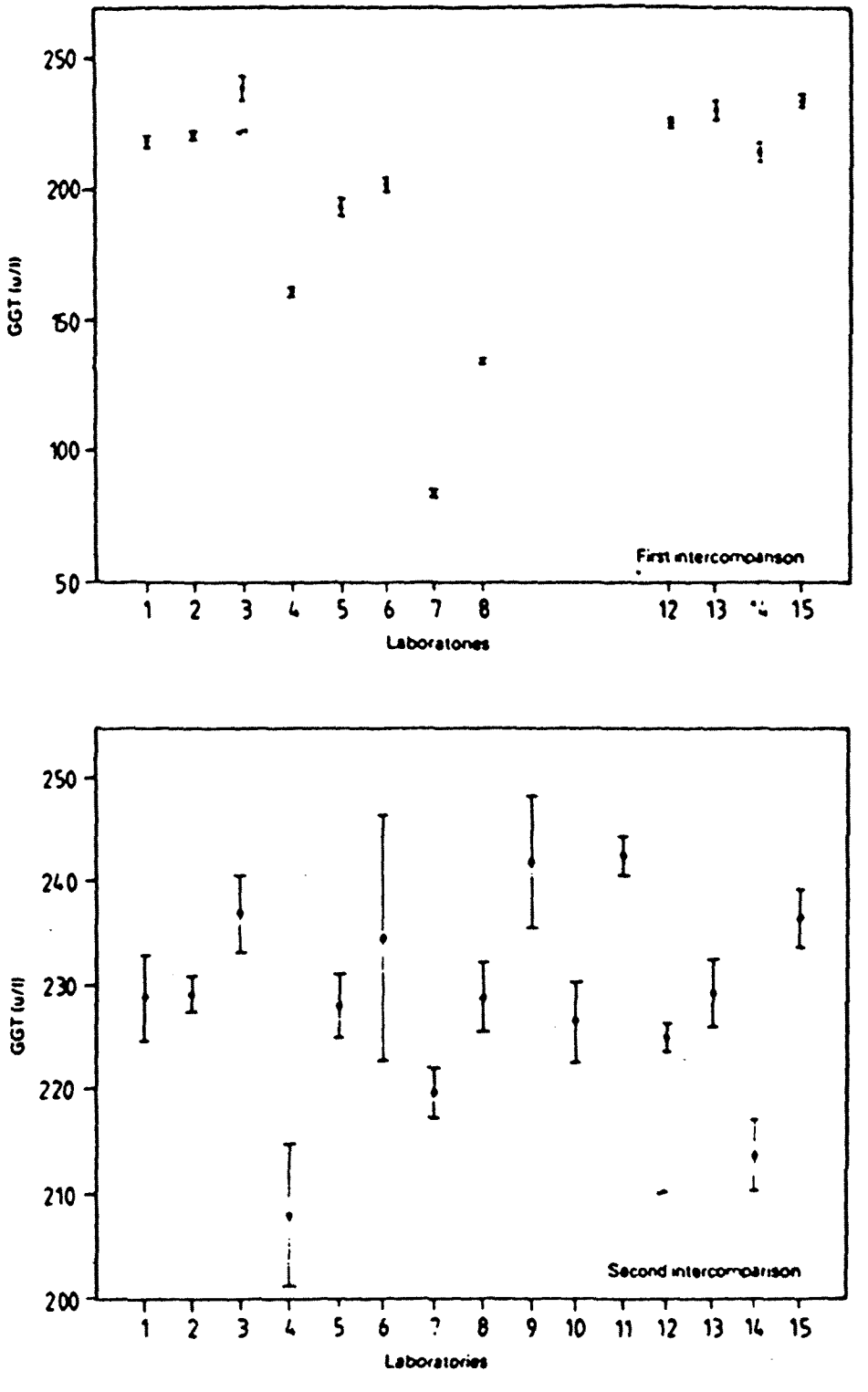


Figure 10 a) – Successive results for the determination of γ-glutamyltransferase in albumin : First and second intercomparisons

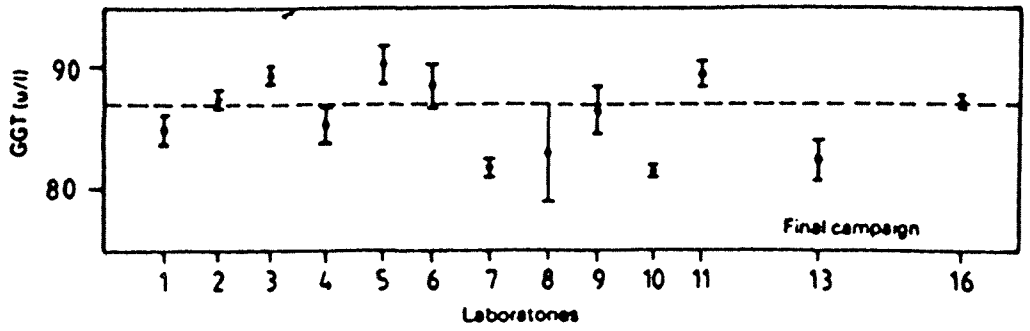


Figure 10 b) — Successive results for the determination of γ-glutamyltransferase in albumin : Final campaign

Appendix B

Participating Laboratories

LEGEND
(Appendix B)

OBS = Reported Result

METH = Method Number
- 1 = Microwave/Atomic Absorption Spectrometry
- 2 = Hotplate/Atomic Absorption Spectrometry
- 3 = Microwave/Inductively Coupled Plasma Emission Spectrometry
- 4 = Hotplate/Inductively Coupled Plasma Emission Spectrometry
- 5 = Laboratory XRF

LAB = Code Assigned to Laboratory

ANAL = Analytical Method
- AA = Atomic Absorption Spectrometry
- ICP = Inductively Coupled Plasma Emission Spectrometry
- XRF = Laboratory XRF

EXTR = Extraction Method
- NIO = NIOSH Method 7082
- EPA = EPA/AREAL Method

List of Participating Laboratories by Method

OBS	METH	LAB	ANAL	EXTR
1	1	10	AA	EPA
2	1	11	AA	EPA
3	1	12	AA	EPA
4	1	13	AA	EPA
5	1	14	AA	EPA
6	1	15	AA	EPA
7	1	16	AA	EPA
8	2	20	AA	NIO
9	2	21	AA	NIO
10	2	22	AA	NIO
11	2	23	AA	NIO
12	2	24	AA	NIO
13	2	25	AA	NIO
14	2	26	AA	NIO
15	2	27	AA	NIO
16	2	28	AA	NIO
17	3	30	ICP	EPA
18	3	31	ICP	EPA
19	3	32	ICP	EPA
20	3	33	ICP	EPA
21	3	34	ICP	EPA
22	3	35	ICP	EPA
23	3	36	ICP	EPA
24	3	37	ICP	EPA
25	3	38	ICP	EPA
26	4	40	ICP	NIO
27	4	41	ICP	NIO
28	4	42	ICP	NIO
29	4	43	ICP	NIO
30	4	44	ICP	NIO
31	4	45	ICP	NIO
32	4	46	ICP	NIO
33	4	47	ICP	NIO
34	4	48	ICP	NIO
35	4	49	ICP	NIO
36	5	50	XRF	N/A
37	5	51	XRF	N/A
38	5	52	XRF	N/A
39	5	53	XRF	N/A
40	5	54	XRF	N/A
41	5	55	XRF	N/A
42	5	56	XRF	N/A

LABORATORIES PARTICIPATING IN EPA/RTI ROUND-ROBIN

Alpha Analytical Labs
8 Walkup Drive
Westboro, MA 01581
Ms. Kathleen O'Brien
(508) 898-9220

American Medical Laboratories
11091 Main Street
Fairfax, VA 22030
(703) 802-6900

Azimuth, Inc.
9229 University Blvd.
Charleston, SC 29418
(803) 553-9456

Clayton Environmental Consultants
1252 Quarry Lane
Pleasanton, CA 94566
Mr. Ron Peters
(510) 426-2641

Clayton Environmental Consultants
22345 Roethel Drive
Novi, MI 48050
Ms. Ellen Coffman
(313) 344-1770

EOHSI
681 Frelinghuysen Road
P. O. Box 1179
Piscataway, NJ 08855
Dr. Clifford Weisel
(908) 932-0154

ESA Laboratories, Inc.
Industrial Hygiene Analytical Laboratory
43 Wiggins Avenue
Bedford, MA 01730
Mr. Paul Ullucci
(617) 275-0100

Galson Technical Services
Industrial Hygiene Laboratory
6601 Kirkville Road
East Syracuse, NY 13057
Ms. Mary Withrow
(315) 432-0506

IT
5103 Old William Penn Hwy.
Export, PA 15632
Mr. Lyle Linsenbigler
(412) 731-8806

Keystone NEA Environmental Services
12242 S.W. Garden Place
Tigard, OR 97223
Mr. Thomas Nadermann
(503) 624-2773

Lawrence Livermore National Laboratory
Hazards Control Laboratory
7000 East Ave. P. O. Box 808 L-383
Livermore, CA 94550
Mr. Ray Szidom
(415) 423-7348

Liberty Mutual Insurance Company
Industrial Hygiene Laboratory
71 Frankland Road
Hopkinton, MA 07148
Mr. Ken Muzal
(503) 435-9061

Maryland Department of Health and Mental Hygiene
Division of Clinical Lab Services
Lead Lab, Room 509
201 W. Preston
Baltimore, MD 21201
Ms. Marilyn Gallagher
(410) 225-6184

Massachusetts State Laboratory Institute
Environmental Lead Laboratory/Room 311
305 South Street
Jamaica Plain, MA 02130
Ms. Phyllis Madigan
(617) 522-3700, Ext. 363

Materials Analytical Services
2418 Blue Ridge Road, Suite 105
Raleigh, NC 27607
Mr. Don Porterfield
(919) 881-7708

Metro Denver Wastewater Reclamation
6450 York Street
Denver, CO 80229
Ms. Molly Lee Castleberry
(303) 289-5941

Midwest Research Institute
425 Volker Blvd.
Kansas City, MO 64110
Dr. John Stanley
(816) 753-7600, Ext. 160

National Loss Control Service Corporation
Environmental Sciences Laboratory
Rt. 22 and Kemper Ctr.
Long Grove, IL 60049
Ms. Joan A. Wronski
(800) 323-9585

NIOSH
Alice Hamilton Laboratories, R-8
4676 Columbia Parkway
Cincinnati, OH 45226
Mr. Peter Eller
(513) 841-4256

OWMC Laboratory
555 North Service Road
Burlington, Ontario L7L5H7
Mr. Joe Lesko
(416) 332-6711

Pennsylvania Department of Environmental Resources
712 Maryland Avenue
Erie, PA 16505
Mr. Gary Manczka
(814) 871-4291

Research Triangle Institute
Analytical and Chemical Sciences
P. O. Box 12194
Research Triangle Park, NC 27709
Dr. Margaret Martin-Goldberg
(919) 541-7211

Roche Analytics Laboratory
P. O. Box 25249
Richmond, VA 23260
Ms. Sue Salkin
(800) 888-8061

SRI International
Physical and Analytical Chemistry Laboratory
333 Ravenswood Avenue
Menlo Park, CA 94025-PS-177
Ms. Helen Parish
(415) 859-6177

Swanson Environmental
3150 Brookfield Road
Brookfield, WI 53045
Ms. Rosemary Dinen
(414) 783-6111

UEC Laboratories
4000 Tech Center Drive, MS#15
Monroeville, PA 15146
Mr. Mark Banister
(412) 825-2400

University of Cincinnati Medical Center
Department of Environmental Health
Kettering Laboratory Analytical Section
3223 Eden Ave., ML-56
Cincinnati, OH 45267-0056
Ms. Sandy Roda
(513) 558-1705

U.S. AEHA
Bldg. E, 2100
APGEA
HSHB-ML-R-M
Aberdeen Proving Ground, MD 21010
Mr. Dave Rosak
(410) 671-2619

U.S. Department of Labor/Salt Lake Technical Center
P. O. Box 65200
Salt Lake City, UT 84165-0200
or
1781 S. 3rd West
Salt Lake City, UT 84115
Dr. Ray Abel
(810) 524-4270

U.S. Environmental Protection Agency, EMSL/Las Vegas
Environmental Programs Office
Lockheed ESC
1050 E. Flamingo Road
Suite 120
Las Vegas, NV 89119
Dr. Harold Vincent/Ms. Dawn Boyer
(702) 798-2129

U.S. Environmental Protection Agency, EMSL/Las Vegas
Methods Research Branch
944 E. Harmon Street
Las Vegas, NV 89119
Mr. Thomas Hinners
(702) 798-2140

U.S. Environmental Protection Agency
Region VII
25 Funston Road
Kansas City, Kansas 66115
Mr. Raymond Paus
(913) 551-5155

Wisconsin Occupational Health Laboratory
Department of Hygiene
979 Jonathon Drive
Madison, WI 53713
Mr. Terry Burke
(608) 263-6550

Appendix C

Standard Operating Procedures

Appendix C-1

AAS/ICP SOP - "Standard Operating Procedures for Lead in Paint by Hotplate- or Microwave-based Acid Digestions and Atomic Absorption or Inductively Coupled Plasma Emission Spectrometry"

RESEARCH TRIANGLE INSTITUTE

RTI

Center for Environmental Measurements and Quality Assurance

March 18, 1992

Ms. Kathleen O'Brien
Alpha Analytical Labs
8 Walkup Drive
Westboro, MA 01581

Digestion Methods: NIOSH 7082 and EPA/AREAL
Analysis Method: ICP

Dear Ms. O'Brien:

Please find enclosed the RTI report, "Standard Operating Procedures for Lead in Paint by Hotplate- or Microwave-based Acid Digestions and Atomic Absorption or Inductively Coupled Plasma Emission Spectrometry." The report describes protocols to be followed for digestion of paint and dust samples by the the NIOSH 7082 (Hotplate) and EPA/AREAL (Microwave) methods for the EPA/RTI round robin. Paint and dust samples are being shipped under separate cover.

Once again, thank you for your participation in the round robin.

Sincerely,

Emily Williams

Emily Williams

Post Office Box 12194 Research Triangle Park, North Carolina 27709-2194
Telephone 919 541-6914 Fax: 919 541-5929

United States
Environmental Protection
Agency

Atmospheric Research and Exposure
Assessment Laboratory
Research Triangle Park, NC 27711

Environmental Criteria
and Assessment Office
Research Triangle Park, NC 27711

September 1991

Research and Development & Pesticides and Toxic Substances

EPA 600/8-91/213

EPA

Standard Operating Procedures for Lead in Paint by Hotplate- or Microwave-based Acid Digestions and Atomic Absorption or Inductively Coupled Plasma Emission Spectrometry

PB92-114172
September 1991

Standard Operating Procedures for Lead in Paint by Hotplate- or Microwave-based Acid Digestions and Atomic Absorption or Inductively Coupled Plasma Emission Spectrometry

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Prepared by

D. A. Binstock
D. L. Hardison
P. M. Grohse
W. F. Gutknecht

Center for Environmental Measurements and Quality Assurance
Research Triangle Institute
Research Triangle Park, North Carolina 27709-2194

EPA Contract No. 68-02-4550
RTI Project No. 91U-4699-100

EPA Project Officers:

M. E. Beard
S. L. Harper
D. J. von Lehmden

Atmospheric Research and Exposure Assessment Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Prepared for

Environmental Criteria and Assessment Office
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

TABLE OF CONTENTS

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under EPA Contract No. 68-02-4550 to the Research Triangle Institute. It has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

1.0 PRINCIPLE AND APPLICABILITY

1.1 SCOPE AND APPLICATION

The adverse health effects resulting from exposure of young children to environmental lead has received increasing attention in recent years. Studies have shown that chronic exposure even to low levels of lead can result in impairment of the central nervous system, mental retardation and behavioral disorders. Although young children are at the greatest risk, adults may suffer harmful effects as well.

The major sources of exposure to lead in housing units are thought to be paint, dust and soil. Food, water and airborne lead are also potential sources but are considered to be minor avenues of exposure. Though soil and dust serve as the principle vehicles of direct exposure, lead-based paint is receiving emphasis as the source of lead in these two media and is the focus of this document.

Under Section 302 of the Lead-Based Paint Poisoning Prevention Act, as amended, Public Housing Authorities (PHAs) are required, by 1994, to randomly inspect all their housing projects for lead-based paint[1]. Currently, the device most frequently used for testing in housing is the portable x-ray fluorescence (XRF) spectrometer, which gives rapid results and is non-destructive. However, uncertainty in accuracy and precision of XRF measurements is a major problem, especially at and below the abatement level for paint, i.e., 5000 µg/g or 1 mg/cm^2.[2] Inconclusive XRF measurements currently must be confirmed in the laboratory using a more accurate method such as atomic absorption spectrometry (AAS) or inductively coupled argon plasma emission spectrometry (ICP). This standard operating procedure describes use of these two methods for determination of lead in paint.

1.2 SUMMARY OF METHOD

1.2.1 Sampling and Measurement

Paint chips will be collected in the field according to HUD guidelines.[2] The collection of blank paint film samples will also be performed wherein these blanks consist of non-lead-based paint (as determined by XRF or some other screening technique) collected in the vicinity of the lead-based paint.

Lead in the paint is solubilized by extraction with nitric acid (HNO_3) and hydrogen peroxide (H_2O_2) facilitated by heat (modification of NIOSH 7082)[3], or by a mixture of HNO_3 and hydro-

chloric acid (HCl) facilitated by microwave energy.[4]

The lead content of the sample is measured by atomic absorption spectrometry (AAS) using an air-acetylene flame, the 283.3 or 217.0 nm lead absorption line and the optimum instrumental conditions recommended by the manufacturer. Alternatively the lead is measured by inductively coupled argon plasma emission spectrometry (ICP), the 220.35 nm emission line, and the optimum instrumental conditions recommended by the manufacturer.

1.2.2 Range, Sensitivity and Method Discrimination Limit

The values given below are typical of the method's capabilities. Absolute values will vary for individual situations depending on the complexity of the paint sample, the type of instrument used, the lead line and operating conditions.

1.2.2.1 Range--

Using the NIOSH method (without additional dilutions), a typical sample analysis range for AAS is 1000 - 20,000 µg Pb/g (0.10 - 2%) assuming the instrument is linear up to 20 µg/mL, while for ICP, the typical range is 100 - 200,000 µg Pb/g (0.010 - 20%) assuming the instrument is linear up to 200 µg/mL. A paint sample mass of 0.1 g and a solution volume of 100 mL is assumed for determination of both of these ranges.

Using the microwave method (without additional dilutions), a typical range for AAS is 200 - 4,000 µg Pb/g (0.020 - 0.4%) while for ICP, the typical range is 20 - 40,000 µg Pb/g (0.002 - 4.0%). The upper linear ranges and sample mass are assumed to be the same as presented in the previous paragraph; the solution volume is assumed to be 20 mL. In order to analyze high levels of lead by AAS in samples prepared using the microwave method, the samples will need to be diluted. A 1 to 5 dilution will extend the linear range to 20,000 µg Pb/g (2.0%).

1.2.2.2 Sensitivity--

Typical AAS sensitivities for 1 percent change in absorption (0.0044) absorbance units) are 0.2 and 0.5 µg Pb/mL for the 217.0 and 283.3 nm lines, respectively. ICP sensitivity is a function of the photocurrent integration time as well as other instrumental parameters. However, an indication of ICP sensitivity at a given wavelength is the ratio of net analyte intensity to background analyte intensity, I_n/I_b. For the 220.35 nm line, a reasonable

value for this ratio is 50 - 100, which would result in a detection limit of approximately 0.050 µg/mL (50 ppb).[5]

1.2.2.3 Method Discrimination Limit (MDL)--

A typical MDL for AAS is 500 µg Pb/g and for ICP is 50 µg Pb/g using the HNO_3/H_2O_2 hotplate method and for AAS is 100 µg Pb/g and for ICP is 10 µg Pb/g using the HNO_3/HCl microwave method. The smallest mass of lead that can be detected by flame AAS (assuming a solution volume of 100 mL) is 100 µg while the smallest mass of lead that can be detected by ICP (assuming a volume of 100 mL) is 10 µg. These values were calculated as equivalent to twice the within-laboratory standard deviation obtained for the lowest measurable lead concentration in a test of the method.[6,7] A paint sample weight of 0.1 gm is assumed.

1.2.3 Interferences

Interferences for AAS and ICP can be manufacturer and model specific. The following are general guidelines.

1.2.3.1 AAS--

1.2.3.1.1 Chemical Interferences--Chemical interferences, that is interactions between molecular and/or ionic species during the absorption process, are not expected and therefore no correction for chemical interference is given here. If the analyst suspects that the sample matrix is causing chemical interference, the interference must be verified and corrected by carrying out the analysis with and without the method of standard additions.[7]

1.2.3.1.2 Light Scattering--Nonatomic absorption or light scattering, produced by high concentrations of dissolved solids in the sample, can produce a significant interference, especially at low lead concentrations. The interference is generally greater at the 217.0 nm line than at the 283.3 nm line. Light scattering interferences can be corrected instrumentally. Since the dissolved solids can vary depending on the origin of the sample, the correction may be necessary, especially when using the 217.0 nm line. Dual beam instruments with a continuum source give the most accurate correction. A less accurate correction can be obtained by using a nonabsorbing lead line that is near the lead analytical line. Information on use of these correction techniques can be obtained from instrument manufacturers' manuals.

If the instrumental correction is not feasible, the effects of the interference can be eliminated through a preliminary separation of the lead from the sample extract. The lead is complexed by ammonium pyrrolidinecarbodithionate and the complex then extracted into methyl isobutyl ketone.[8] The complex-ketone solution is then analyzed directly by atomic absorption spectrometry.

1.2.3.2 ICP--

1.2.3.2.1 Spectral interference--The efficient excitation of sample constituents at high temperature results in the possibility of spectral overlap interferences. A mathematical correction can be applied for the interference if the interfering element and the magnitude of the interference are determined. As an alternative, an interference-free line may be chosen if the line exhibits an adequate detection limit. Background shifts due to stray light, line broadening and recombination continuum and other less well-defined sources, require correction by background measurement near the analysis line. This correction normally is done dynamically within the instrument.

1.2.3.2.2 Physical interferences--Paint digest samples may contain species that affect the efficiency of nebulization with respect to standards when matrix matching is not possible. The existence of physical interferences may be checked for by using the method of standard additions. It has been observed that the high concentrations of dissolved materials in paints may depress the lead values. This effect can be tested by analyzing a set of serial dilutions of the original digest. An increase in the value (properly corrected for the dilution) indicates a matrix effect.

1.2.3.3.3 Chemical interferences--Chemical interferences, that is, interactions between molecular and/or ionic species during the emission process, are insignificant for ICP because of the completeness of destruction of the sample by the high energy of the plasma.

1.2.4 Precision and Bias

Precision of sampling of paint chips is principally dependent upon the number of layers of paint in the chip and the variability in the thickness of these layers, some of which may contain more lead than others. No typical value for sampling precision has been established.

The combined extraction-analysis relative standard deviations are as follows:[7]

HNO_3/H_2O_2 Hotplate Extraction	
ICP	6 - 10% (at >300 µg Pb/g)
AA	4 - 8% (at >1000 µg Pb/g)

HNO_3/HCl Microwave Extraction	
ICP	2 - 6% (at >300 µg Pb/g)
AA	2 - 4% (at >1000 µg Pb/g)

Single laboratory experiments indicate that there is no significant difference in lead recovery between the hotplate and microwave extraction procedures, and recovery of lead from synthetic paint samples and NBS SRM 1579 (lead in paint) was found to be greater than 90 percent in an interlaboratory study.[7]

2.0 APPARATUS

2.1 SAMPLING

The paint sample collection apparatus is described in Section A.5.3.1. of the HUD Guidelines.[2]

2.2 INSTRUMENTATION

2.2.1 Atomic Absorption Spectrophotometer

Flame atomization spectrophotometer equipped with lead hollow cathode or electrodeless discharge lamp. Perkin Elmer Model 603 or equivalent may be used.

2.2.1.1 Acetylene--

The grade recommended by the instrument manufacturer should be used. Change cylinder when pressure drops below 50 - 100 psig.

2.2.1.2 Air--

Filtered to remove particulate, oil and water.

2.2.2 Alternatively, Inductively Coupled Argon Plasma Emission Spectrometer

Computer-controlled plasma emission spectrometer with background correction and radio-frequency generator. Leeman Labs Plasma Spec ICP 2.5 or equivalent may be used.

2.2.2.1 Argon Gas Supply--

Ensure that adequate argon, water and electrical power are available. Liquid argon is the most desirable source of argon, especially for daily use from a cost and labor perspective. If gas is used, ensure adequate purity.

2.2.2.2 Cooling Water--

Recirculating or fresh water that meets flow rate and temperature specifications.

2.2.3 Hotplate

Surface temperature, 140°C.

2.2.4 Alternatively, Microwave Digestion System

Nominal 600 watts power. Includes turntable, 120 mL Teflon vessels and Capping Station. CEM Corporation MDS-81D or equivalent may be used. The power available for heating is to be evaluated weekly. This quality control function is performed to determine that the microwave has not started to degrade and that absolute power settings (watts) may be compared from one microwave unit to another.

This power evaluation is accomplished by measuring the temperature rise in 1 kg (1.0 liter) of water exposed to microwave radiation for a fixed period of time.[9]

The water is placed in a Teflon® beaker and stirred before measuring the temperature. The beaker is circulated continuously through the field for 2 minutes with the unit at full power. The beaker is removed, the water vigorously stirred, and the final temperature recorded. The final reading is the maximum temperature reading after the energy exposure. These measurements should be accurate to $\pm$ 0.1°C and made within 30 sec of the end of heating.

The absorbed power is determined by the following relationship

$$P = \frac{(K)\ (Cp)\ (m)\ (\Delta T)}{t}$$

P = the apparent power absorbed by the sample in watts (W). ($W = Joule \cdot sec^{-1}$)

K = the conversion factor for thermochemical calories$\cdot sec^{-1}$ to W (=4.184)

Cp = the heat capacity, thermal capacity, or specific heat ($cal \cdot g^{-1} \cdot °C^{-1}$), of water

m = the mass of the water sample in grams (g).

ΔT = Tf, the final temperature minus TI, the initial temperature (°C), and

t = the time in seconds (s).

Using 2 minutes and 1 Kg of distilled water, the calibration equation simplifies to: $P = (\Delta T)(34.87)$.

The microwave user can now relate power in watts to the percent power setting of the unit.

2.2.5 Apparatus - HNO_3/H_2O_2 Hotplate Digestion

Beakers: Phillips, 125 mL or Griffin, 50 mL with watchglass covers.

Volumetric Flasks: 200 and 100 mL.

Assorted Volumetric Pipets: As needed.

Bottles with caps: Linear Polyethylene, 100 mL.

NOTE: Only borosilicate, Class A glassware is to be used. Also, before use, all labware should be scrupulously cleaned. The recommended procedure is:

1. Wash with hot, laboratory detergent solution or ultrasonicate with laboratory detergent solution.
2. Rinse and then soak a minimum of 4 hours in 50% V/V nitric acid.
3. Rinse 3 times with doubly deionized water.

2.2.6 Apparatus - HNO_3/HCl Microwave Method

Centrifuge: International Equipment Company Model UV or equivalent.

Centrifuge Tubes: Oak Ridge 30 mL polysulfone tube, polypropylene screw closure, Nalgene 3115-0030 or equivalent.

Pipette, Automatic Dispensing Class A: SMI Incorporated Unipump 200 or equivalent.

Shaker, Mechanical: Eberback Corporation 6460 or equivalent.

2.2.7 Reagents - HNO_3/H_2O_2 Hotplate Digestion

Nitric Acid: Concentrated, spectrographic grade

Nitric Acid, 10% (W/V): Add 100 mL concentrated nitric acid to 500 mL deionized water; dilute to 1L.

Hydrogen Peroxide: 30% H_2O_2, W/W, ACS reagent grade.

Doubly Deionized Water: Building water passed through a Polymetrics, 3 cartridge system or equivalent, then through a Millipore Corporation Milli-Q deionizer or equivalent, and having a minimum of 15 megohm-cm resistivity.

2.2.8 Reagents - HNO_3/HCl Microwave Digestion

Doubly Deionized Water: Building water passed through a Polymetrics, 3 cartridge system or equivalent, then through a Milli-Q deionizer or equivalent, and having a minimum of 15 Megohm-cm resistivity.

Hydrochloric Acid: Concentrated, ACS reagent grade.

Nitric Acid: Concentrated, spectrographic grade.

Extraction Solution: In a 1 liter volumetric flask, combine in order and mix well: 500 mL doubly deionized water, 55.5 mL of concentrated spectrographic grade nitric acid (16.0 N) and 167.5 mL of concentrated hydrochloric acid (12.3 M). Cool and dilute to 1 liter with doubly deionized water.

CAUTION: Nitric Acid and hydrochloric acid fumes are toxic. Prepare in a well ventilated fume hood.

2.2.9 Reagents - Measurement

Master Stock Solution: 1000 µg Pb/mL. Commercial standard; alternatively, weigh out 1.5985 g ACS reagent grade $Pb(NO_3)$ that has been dried for two hours at 110°C and dissolve in 200 mL water in 1 L volumetric flask. Add 10 mL concentrated HNO_3 and dilute to volume with water. Store in a linear polyethylene or Teflon bottle. Stable - one year.

3.0 PROCEDURE

3.1 SAMPLE PREPARATION

Final results may be reported in area concentration (mg/cm^2) or mass concentration (µg/gm). If area concentration is desired, be sure that areas are provided for each paint chip. Then proceed to weigh each total chip sample; only a fraction will be taken for analysis and final concentration will be determined by relating fractional mass to total mass.

Cut the paint chips into small pieces using a sharp blade[2], or alternatively, crush them in a beaker using a glass rod. The sample may be further ground to a fine powder using a mortar and pestle. Alternatively, a small motorized hammermill or other grinding device may be used. Reducing the sample to a fine powder further assures that the extraction methods will be acceptably efficient.

3.2 SAMPLE EXTRACTION

3.2.1 HNO_3/H_2O_2 Hotplate Extraction

Weigh out 0.1 g (nearest milligram) of sample into a 50 mL beaker or 125 mL Phillips beaker. Add 3 mL concentrated HNO_3 and 1 mL 30% H_2O_2 and cover with a watchglass. Start a reagent blank at this step. Heat on a hotplate (140°C) until most of the acid has evaporated. Remove the sample from the hotplate and allow it to cool. Repeat this process two more times using 2 mL concentrated HNO_3 and 1 mL 30% H_2O_2 each time. Finally, heat on a 140°C hotplate until the solution is near dryness.

Rinse the watchglass and walls of the beaker with 3 to 5 mL 10% HNO_3. Allow the solution to evaporate gently to dryness. Cool each beaker and add 1 mL concentrated HNO_3 to the residue. Swirl to dissolve soluble species. Next perform filtration, which should take place under the hood. Use a wash bottle filled with deionized water for rinsing. Set up the glass funnels over 100 mL prelabeled volumetric flasks. In each funnel, place a folded Whatman #54 filter paper. Before filtering, wet filter paper and rinse glassware with about 20 - 30 mL of water. Discard waste rinse. To filter, decant the liquid from the sample first, then pour the solids onto the filter. Once this has drained, wash the beaker with 3 small (3 mL) portions of water, adding each wash to the filter paper. Rinse the filter paper with 3 small (3 mL) portions of water. After the filter paper is thoroughly drained, it is discarded. Rinse the glass funnel with one small portion of water. Dilute to volume with deionized water. The sample is 1% in nitric acid. Caution: Nitric acid fumes are toxic.

3.2.2 HNO_3/HCl Microwave Extraction

Weigh out 0.1 gram (nearest milligram) of sample into a 30 mL polysulfone Oak Ridge centrifuge tube. Add 10 mL of extraction solution (Section 2.2.8) using Class A automatic dispensing pipette

(SMI Incorporated Unipump 200 or equivalent). Cap the tube tightly.

Pipette 31 mL of double deionized water into a 120 mL Teflon microwave digestion vessel. Place an Oak Ridge centrifuge tube containing the sample in the 120 mL Teflon microwave digestion vessel. Place a safety valve and cap on the vessel and tighten the cap using the capping station. Fill the microwave turntable with 12 vessels containing the centrifuge tubes. Put the filled turntable in the microwave oven; activate the "on" switch and the "turntable" switch. Set the exhaust fan to maximum speed. Program the microwave oven for a time of 23 minutes and a power of 81% (522 watts) and press the "start" button.

At the end of the program, remove the turntable containing the microwave vessels and cool it in tap water for 10 minutes. Open the microwave vessels and discard the water they contain. Open the Oak Ridge centrifuge tubes and add 10 mL of doubly deionized water using a Class A automatic dispensing pipette (SMI Incorporated Unipump 200 or equivalent). Cap the tubes tightly and mechanically shake 5 minutes. Centrifuge 25 minutes at 2000 RPM (International Equipment Company Model UV or equivalent). Open the centrifuge tubes and decant or pipette off the clear solution into an acid cleaned 20 mL scintillation vial for analysis. Use a sample volume of 20 mL to calculate analytical results. The sample is 1.03 M in hydrochloric acid and 0.45 M in nitric acid.

NOTE: The sample solutions may need to be further diluted to stay within the linear calibration range.

4.0 ANALYSIS

4.1 AAS-CALIBRATION

4.1.1 Working Standard, 20 µg Pb/mL

Prepare by diluting 2.0 mL of the 1000 µg/mL master stock solution (Section 2.2.9) to 100 mL in 1% HNO_3 if the HNO_3/H_2O_2 hotplate extraction was used, or 0.45 M HNO_3/1.03 M HCl if the HNO_3/HCl microwave method was used. The working standard should be prepared at least weekly; daily preparation is preferred.

4.1.2 Calibration Standards

Prepare daily by diluting the working standard, as indicated below with acid solution to match the sample matrix (1% in HNO_3 or 0.45 M HNO_3/1.03 M HCl). Other lead concentrations may be used.

Volume of 20 µg Pb/mL working standard, mL	Final volume, mL	Concentration, µg Pb/mL
0	100	0
5.0	100	1.0
25.0	100	5.0
50.0	100	10.0
100.0	100	20.0

4.1.3 Calibration Curve

The calibration curve may be manually plotted, determined with a hand calculator using linear regression analysis or calculated automatically. Some automatic systems will simply display the analysis results calculated by the internal electronics and/or computer. Other, more complex systems will allow selection of the curve fitting function (e.g., linear, polynomial, segmental) and provide values for the function constants (e.g., slope and intercept for the linear function $y = mx + b$). When first calibrating the system or after any significant change to or work on the instrument, a manually plotted standard curve should be compared to the standard curve calculated from the mathematical function. Any difference in the curves of more than 10% needs to be investigated and corrective action taken. Such action may include selection of a different curve fitting function.

4.2 ICP - CALIBRATION

4.2.1 Working Standard, 100 µg/mL

Prepare by diluting of 10.0 mL of the 1000 µg/mL master stock solution to 100 mL in 1% HNO_3 if the HNO_3/H_2O_2 hotplate extraction was used or 0.45 M HNO_3/1.03 M HCl if the HNO_3/HCl microwave method was used. The working standard should be prepared at least weekly; daily preparation is preferred.

4.2.2 Calibration Standards

Normally 2 to 5 standards are used for ICP calibration. Typical concentrations are shown below. Prepare daily by diluting the working standard, as indicated below.

Volume of 100 µg Pb/mL working standard, mL	Final volume, mL	Concentration, µg Pb/mL
0	100	0
1.0	200	0.5
3.0	100	3.0
10.0	100	10.0
30.0	100	30.0
100.0	100	100

Higher lead concentrations may be used as long as linearity of response is maintained.

4.2.3 Calibration Curve

The calibration curve (integrated photocurrent [or equivalent] vs concentration) will be calculated automatically. When first calibrating the system or after any significant change to or work on the instrument, a manually plotted standard curve should be prepared and then compared to the standard curve calculated by the system. Any difference in the curves of more than 10% needs to be investigated and corrective action taken.

4.3 QUALITY CONTROL PRIOR TO SAMPLE ANALYSIS

Quality control is necessary to assure that resulting data are of adequate quality. Several tests are to be performed prior to sample analysis. These are as follows:

4.3.1 Blank Check

Laboratory or reagent blanks are analyzed to determine the background or contamination levels. Contamination levels above detection limit must be accounted for and eliminated, if possible, before proceeding with sample analysis. Field blanks (that is, paint samples testing very low in the field) that show lead levels well above levels for "lead-free" paint, that is, above 500 - 1000 µg Pb/g, indicate possible cross contamination of samples. As with laboratory blanks, high lead values for field blanks must be accounted for and corrective action taken, if necessary.

4.3.2 Matrix Interference Check

Chemical and/or physical interferences may cause error. These are checked by the methods of standard additions and sample dilution.

4.3.2.1 Method of Addition Check--

Aliquots of digests representing each source of paint samples are spiked with lead solution after initial analysis to approximately double the concentration. The recovery must be within 80% to 120% of the known value. The spike addition should produce a minimal level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected. The use of a standard-addition analysis (MSA) procedure can usually compensate for this effect. If an MSA procedure does not produce acceptable recovery, then the digestion procedure must be regarded as suspect.

CAUTION: The standard-addition technique does not detect coincident spectral overlap. If suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

4.3.2.2 Dilution Check--

It has been observed that the high concentrations of dissolved materials in paints depress the values measured by ICP. The effect must be tested for by analyzing a set of serial dilutions of the original digest, e.g., 1:10, 1:25, 1:100. An increase in the value (properly corrected for the dilution) indicates a matrix effect. Such a dilution test should be performed for each new matrix type. The final dilution ratio used will be limited by the lead concentration, which should be between 1 and 10 ppm for optimum measurement.

4.3.3 ICP Interfering Element Check

When lead in paints is being measured by ICP, it is important to be aware of the potential for spectral interferences due to the existence of potentially high levels of interferences (e.g. Ti, Al, Cr, etc). It is important to periodically analyze Interfering Element Check Samples that contain known high levels (200 - 1000 ppm) of each suspected interfering element. Such solutions are available from a variety of vendors. Once the solutions are analyzed, the data must be evaluated to determine the existence of a false lead value attributed to the interferences that are more than 2 x the solution detection limit. If the false values do exceed this criteria, an interfering element correction factor (F_{IEC}) must be determined as follows:

$$F_{IEC} = \frac{\text{False analyte signal}}{\text{Concentration of Interferant}}$$

For example - 1000 ppm of aluminum causes an approximately false lead signal of 0.250 ppm (7 x DL_{Pb})

Therefore, F_{IEC} = (0.25/1000)=0.00025

This value is used to correct lead data in the presence of high aluminum. The interfering element identified in the above manner is therefore added to the analytical program. This procedure must be applied to all potential interfering elements.

4.3.4 Calibration Check Samples

A check sample prepared from an independent master stock solution must be run after standardization to determine the accuracy of the simple aqueous standards. The concentration of the check sample should be approximately 75% of the highest calibration standard. Agreement must be within ±5% of expected or a recalibration must be performed, possibly with fresh standards.

4.4 QUALITY CONTROL DURING ANALYSIS

During the course of analysis, the following quality control activities are to be performed.

4.4.1 Reagent Blanks

A reagent blank (extraction reagent carried through entire analytical process) is to be run after every 20 samples. A sudden increase would indicate a contamination problem.

4.4.2 Calibration Checks

High and low, independently prepared check samples are to be run alternately after every 10 samples to determine that calibration has not drifted. If a change of more than 10% is measured, the system must be recalibrated and all samples run since the last calibration check rerun.

The results should be plotted on a control chart at the end of each sample analysis session, although real-time checking is preferred.[10] The analysis is concluded to be out of control if any one or more of the following is met.

1. One or more points outside of the control limits.

2. A run of at least eight points, where the type of run could be either a run up or down, a run above or below the center line, or a run above or below the median.

3. Two of three consecutive points outside the 2-sigma warning limits but still inside the control limits.

4. Four of five consecutive points beyond the 1-sigma limits.

5. An unusual or nonrandom pattern in the data.

6. One or more points near a warning or control limit.

4.4.3 Duplicates

Analyze one duplicate samples for every 20 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process. The acceptance criteria for precision of the duplicate analyses varies with proximity of the analytical result to the detection limit and is as follows:

Average Analyte Concentration Concentration (Multiples of Detection Limit	Maximum Acceptable, Average Relative Percent Difference
0 - 2	200%
2 - 10	17.3%
>10	8.6%

Where Average Relative Percent Difference =

$((X_1 - X_2)/((X_1 - X_2)/2)) \times 100$

These values result in estimates of the 95% confidence intervals for the method of (1) $\pm$ 30% for concentrations 2 - 10 x the method discrimination limit, and (2) $\pm$ 15% for concentrations > 10 x the method discrimination limit.[11] If unacceptable precision is obtained, corrective action is to be taken including review of all original data and calculations and possible analysis of a second duplicate sample.

4.4.4 Standard Reference Materials (SRMs)

Depending on the matrix, a standard reference material should be analyzed once per sample batch or, at a minimum, once per day to check the entire extraction/analysis procedure. Lead recovery should be within 90 to 110% of the known value. An appropriate reference material for lead at the present time is NIST 1579 Powdered Lead-Based Paint at 11.87%. Additional paint standards having lower lead concentrations will be available from NIST

sometime in 1992. Plot results on a control chart as outlined in Section 4.4.2. If the sample is out of control, sources of error must be identified and appropriate corrective action taken.

4.5 SAMPLE DETERMINATION

4.5.1 AAS

Most pertinent startup procedures may be found in the manufacturer's operation manual. The operator should be reasonably familiar with the operation manual regarding basic operation and safety. However, these procedures are outlined below.

1. Turn on the power and install the appropriate lamp and burner head.
2. Set the source lamp current to proper value.
3. Set the slit to the proper value. Set the wavelength to proper value and peak the wavelength setting. Align the lamp.
4. Set the control switch to the desired measurement mode (absorption).
5. Turn on and adjust background correction, if available.
6. Select the proper flame and flow rates and ignite the gases according to the manufacturer's procedure manual. The proper flame is listed in the manufacturer's analytical methods manual. Follow manufacturer's recommendations regarding warm up times.
7. Select the desired integration time.
8. Aspirate a blank solution and auto zero the instrument.
9. Aspirate the calibration standards and establish a calibration curve either manually or automatically such that the standards bracket the samples.
10. Run a calibration check sample as described in Section 4.3.4.
11. Aspirate a sample solution and measure the absorbance and/or the concentration.

4.5.2 ICP

1. Ensure that adequate argon, water and electrical power are available. Liquid argon is the most desirable source of argon, especially for daily use from a cost and labor perspective. If gas is used, ensure adequate purity.
2. Adjustment of Nebulizer Spray - See operator's manual for procedure.
3. Ignition of Torch - Check argon supply is on.

4. After startup - Be sure plasma does not flicker or present an orange corona around torch. If the plasma flickers, be sure the spray chamber is draining properly. If the orange corona is observed, make sure that the nebulizer argon is on. Otherwise some residual salt may be present in the nebulizer spray that must be flushed out or the entire spray chamber assembly must be cleaned.

5. Warmup - Allow the instrument to warm up at least 30 minutes before serious analyses are initiated and the standard readings have stabilized.

6. Optical Calibration/Torch Alignment Procedures - Before analytical calibration procedures are performed, it is important to perform the optical calibration procedures and the torch alignment operation. Each of these is described in the operator's manual.

7. Select program that includes wavelength, integration time, number of replicate readings, sample uptake time and rinse time.

8. Aspirate the calibration standards and establish a calibration curve.

9. Run a calibration check sample as described in Section 4.3.4.

10. Aspirate a sample solution and measure the emission signal.

5.0 DATA PROCESSING

5.1 AAS

The absorbance of each sample result is recorded. If the readout is in absorbance, this value is entered into the linear regression equation and the concentration is calculated. Alternately the instrument will provide a direct readout in concentration.

For direct determination, read the element value (µg/mL) from the calibration curve or readout. If dilution of the sample has been performed, then

µg/mL element in the sample = µg/mL in the dilution X D

Where $D = \frac{(\text{mL of aliquot}) + (\text{mL of diluent})}{\text{mL of aliquot}}$

5.2 ICP

The ICP will provide direct readout in concentration. Correction for dilution is made as described in Section 5.1.

5.3 CALCULATION - FIELD SAMPLE CONCENTRATION

5.3.1 Area Concentration

The area concentration of lead in a paint chip is calculated as follows:

$$mg\ Pb/cm^2 = (C_{TS} \times V_{TS} \times M_{OS}/M_{SA})/(1000 \times A_{OS})$$

where C_{TS} = lead concentration in test solution, corrected for dilution, µg Pb/mL

V_{TS} = volume of sample digest solution, mL

M_{OS} = mass of original sample, g

M_{SA} = mass of sample aliquot digested, g

A_{OS} = area of original sample, cm^2

5.3.2 Mass Concentration

The mass concentration of lead in a paint chip is calculated as follows:

$$\mu g\ Pb/g = (C_{TS} \times V_{TS})/M_{SA}$$

where C_{TS} = lead concentration in test solution, corrected for dilution, µg Pb/mL

V_{TS} = volume of sample digest solution, mL

M_{SA} = mass of sample aliquot digested, g

6.0 REFERENCES

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Appendix C-2

Laboratory XRF SOP - "Standard Operating Procedures for Energy Dispersive X-ray Fluorescence Analysis of Lead in Urban Soil and Dust Audit Samples"

RESEARCH TRIANGLE INSTITUTE

Center for Environmental Measurements and Quality Assurance

May 29, 1992

Mr. Thomas Nadermann
Keystone NEA Environmental Services
12242 S.W. Garden Place
Tigard, Oregon 97223

Dear Mr. Nadermann:

Please find enclosed the document, "Standard Operating Procedures for Energy Dispersive X-Ray Fluorescence Analysis of Lead in Urban Soil and Dust Audit Samples," referenced in the letter sent to you with the round robin samples. If your laboratory has established protocols for the analysis of dust, please follow these established protocols. We are including the SOP only as a reference for laboratories that do not have standard procedures for these analyses.

Once again, thank you for your participation in the EPA/RTI round robin for lead-based paint and dust.

Sincerely,

Emily Williams

Emily Williams

Post Office Box 12194 Research Triangle Park, North Carolina 27709-2194
Telephone 919 541-6914 Fax: 919 541-5929

DRAFT

STANDARD OPERATING PROCEDURES FOR ENERGY DISPERSIVE X-RAY FLUORESCENCE ANALYSIS OF LEAD IN URBAN SOIL AND DUST AUDIT SAMPLES

by

Dawn M. Boyer & Daniel C. Hillman
Lockheed Engineering & Sciences Company
Las Vegas, Nevada 89119-3705

Contract No. 68-C0-0049

Project Officer

Harold A. Vincent, Quality Assurance Division
Environmental Monitoring Systems Laboratory
Las Vegas, Nevada 89193-3478

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH & DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
LAS VEGAS, NEVADA 89193-3478

Notice

This document is a preliminary draft. It has not been formally released by the U. S. Environmental Protection Agency policy. It is being circulated for comments on its technical merit and policy implications.

Mention of corporation names, trade names, or commercial products does not constitute endorsement or recommendation for use.

Table of Contents

List of Abbreviations

DL	detection limit
GFAA	Graphite Furnace Atomic Adsorption
ICPAES	Inductively Coupled Plasma Atomic Emissions Spectroscopy
HCV	high calibration verification sample
LCV	low calibration verification sample
LCS	laboratory control sample
MCA	multichannel analyzer
MDL	minimum detection limit
QA	quality assurance
RM	reference monitor
RSD	relative standard deviation
SOP	standard operating procedure
ULADP	Urban Lead Abatement Demonstration Program
XRF	X-ray fluorescence

INTRODUCTION

Lead in the human body, whether at high or low concentration, temporary or long lasting, may result in a broad spectrum of adverse health effects. These effects, sometimes called "lead poisoning" when severe, range from dizziness, hearing impairment, destruction of red blood cells, and delayed cognitive behavior, to convulsions, coma, and death. While lead poisoning can be treated, many of its developmental effects are irreversible.

Young children are the population most at risk from excessive lead exposure due to their physiological development and their frequent contact with lead-contaminated parts of their environment (dust, leaded paint chips, soil, etc.). Lead exposure may result from normal outdoor play activities as well as from indoor contact with paint and contaminated dust which may collect on carpets, floors, and furniture. The human fetus is also part of this high-risk population; lead in the maternal bloodstream may produce toxic fetal effects including reduction in gestational age, birth weight, and mental development[1].

Energy dispersive x-ray fluorescence (XRF) has been identified as an effective analytical tool for measuring lead in solid materials including dust, soil, and paint. XRF advantages are that it quick, precise, cost effective, nondestructive and requires minimal sample preparation. This standard operating procedure (SOP) was designed to provide a method suitable for measuring lead in urban soil and dust audit samples for the Urban Lead Abatement Demonstration Project (ULADP).[2]

1.0 SAMPLE PREPARATION

1.1 Soil Samples- It is assumed that soil samples have previously been reduced to < 60 mesh. This procedure is written assuming an initial sample size of about 20 g.

1.1.1 Homogenization and Subsampling to 5-g Aliquots

Initial Homogenization- Position the two receiving pans under the small riffle splitter. Pour the entire 20-g aliquot from the distribution pan evenly across the baffles of the riffle splitter. Transfer the soil from each receiving pan into the distribution pan and replace the receiving pans under the riffle splitter. Repeat this step five times in succession.

Splitting into 5-g Aliquots- Pour a 20-g aliquot evenly across the baffles of the small riffle splitter. Place the soil from one receiving pan into a plastic bag. Transfer the soil from other receiving pan to the distribution pan and continue splitting as necessary until approximately 5 g of soil occupies each receiving pan. Place the entire contents of the pan into pre-labeled sample container. Repeat the procedure until the entire 20-g sample is split into an even number of 5-g aliquots.

1.2 Dust Samples- It is assumed that soil samples have previously been reduced to < 60 mesh and that the sample size of about 2 g.

1.2.1 Homogenization- Position the two receiving pans under the small riffle splitter. Pour the entire 2-g aliquot from the distribution pan evenly across the baffles of the riffle splitter. Transfer the dust from each receiving pan into the distribution pan and replace the receiving pans under the riffle splitter. Repeat this step five times in succession.

1.3 Loading XRF Sample Cups for Analysis- Pour a 5-g soil aliquot or 2-g dust aliquot into an XRF sample cup and seal with 3.6 μm mylar film.

2.0 ENERGY DISPERSIVE X-RAY FLUORESCENCE ANALYSIS

2.1 Summary - Samples are loaded into the spectrometer and the sample is with irradiated x-rays. The characteristic line spectrum consists of a series of discrete wavelengths, x-ray spectral lines, characteristic of the emitting element and having various relative intensities.

The line spectrum of an element originates when electrons are expelled from inner levels of its atoms, and electrons from levels farther out fall into the vacancies. Each transition constitutes an energy loss which appears as an x-ray photon. The minimum photon energy that can expel an electron from a given level in an atom of a given element is known as the absorption edge of that level of that element. Each element has as many absorption edges as it has excitation potentials[3]

X-ray spectral lines of all elements in the sample are excited and detected simultaneously, then the resulting detector output pulses are separated electronically on the basis of their pulse height.[4] Loose powder samples are analyzed by XRF. The Pb L-beta peak/ Ag Compton peak ratio is calculated. The lead concentration is determined from the ratio and the calibration curve (Ratio vs. Concentration). Quality control is described in Section 1.4.

2.2 Instrument Parameters

Instrument:	Kevex Delta Analyst 770
Sample Form:	Dust (< 60 mesh)
Cup Diameter:	31 mm
Counting Time:	200 sec
X-ray Tube Voltage:	35 KeV
X-ray Tube Current:	3.0 Ma
Secondary Target:	Silver
Analysis Atmosphere:	Air

2.3 Peak Processing Procedure

A.) Acquire the spectrum: This routine begins the acquisition of data into the currently enabled multichannel analyzer (MCA) memory group.

B.) Save the spectrum: This routine save the spectra in a spectrum file.

C.) Process the escape peaks: This routine corrects spectral data for losses due to fluorescence and subsequent escape of silicon K-α x-rays in the detector crystal.

D.) Smooth the spectrum: This routine smooths the spectrum using a pseudo-Gaussian 1:2:1 3-point smoothing correlator.

E.) Deconvolute the Scatter peaks: This routine fits Gaussians to the Compton and Rayleigh peaks, and computes the Compton-to-Rayleigh intensity ratio for the current spectrum.

F.) Save the Compton intensity: This routine save the Compton intensity in a specified file.
G.) Recall the old spectrum: This routine recalls the last spectra in memory prior to any spectral processing.
H.) Process the escape peaks: This routine corrects spectral data for losses due to fluorescence and subsequent escape of silicon K-α x-rays in the detector crystal.
I.) Process the summation peaks: This routine removes undesired sum peaks from spectra, due to trailing-edge pulse pileup during high deadtime acquisition.
J.) Subtract the background: This routine subtracts the background stored in the processing group P2 from the spectrum stored in group P1.
K.) Identify the Pb peak: This routine adds specified elements to the current element list of the current spectrum.
L.) Deconvolute Pb Lβ intensity by integration: This routine extracts intensities by integration.
M.) Clear the background: This routine erases any background presently stored in group P@, whether or not it is being used.[5]

2.4 Calibration and Quantification- The XRF is calibrated by acquiring spectra from a series of urban soil standards with known lead concentrations. Currently we use a series containing 443, 849, 995, 1069, 2455, 3772, and 17993 mg/kg Pb. Acquisition conditions are given in Section 2.2. The Pb Lβ peak and Ag Compton peak are measured from the spectra and the Pb Lβ peak/Ag Compton peak ratios are calculated. A calibration line is calculated using linear regression of the ratio vs. the lead concentration.

2.5 Determination of Unknown Sample Concentration - The Pb Lβ peak and Ag Compton peak are measured from the spectra and the Pb Lβ peak/Ag Compton peak ratios are calculated. Unknown concentrations are determined from the calibration line discussed in Section 2.4.

3.0 QUALITY CONTROL

Laboratory control sample (LCS) - One LCS sample will be prepared and analyzed per group of 20 samples. A LCS is a real sample with a matrix similar to the samples being analyzed which contains a known concentration of lead.

Reference Monitor (RM) - Prior to analysis, a reference monitor sample is measured. It is an in-house synthetic sample containing 1.273% Fe, 1.505% Sb, 1.507% Y, 9.65% Br,

17.69% Na, and 19.89% Cl. The reference monitor intensity provides a standard measure of the x-ray flux that irradiates the samples being analyzed. The reference monitor provides a method of standardizing and/or compensating for changes in the x-ray tube flux.

High Calibration Verification Sample (HCV) - A HCV sample is a real sample containing lead at a concentration near the upper end of the calibration line. It is analyzed after the RM and after the last sample in a run. The concentration of Pb (17993 mg/kg) is at the high end of the range of interest.

Low Calibration Verification Sample (LCV) - A LCV sample is a real sample containing lead at a concentration near the lower end of the calibration line. It is analyzed after HCV sample in a run. The concentration of Pb (443 mg/kg) is at the low end of the range of interest.

Detection limit (DL) Determination - the smallest concentration/amount of a the analyte of interest that can be measured by a single measurement with a stated level of confidence. This must be determined for each new sample matrix.

Minimum Detection Limit (MDL) - the concentration/amount of analyte that gives a net line intensity equal to three times the square root of the background intensity. This must be determined for each new sample matrix.

4.0 LABORATORY SAFETY

Environmental samples often contains hazardous materials and must be handled with respect. Special equipment and facilities are must be used to prevent safety hazards and eliminate cross contamination of space and other samples. Sample preparation must be performed in a fume hood and personnel must wear a dust mask, PVC gloves, and a lab coat.

Personnel engaged in handling hazardous samples undergo initial and periodic medical examinations to insure that they have not contracted medical problems related to the materials with which they are involved.

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Appendix D

Instructions to Laboratories

Appendix D-1

Letter of Instruction to AAS/ICP Laboratories

RESEARCH TRIANGLE INSTITUTE

/RTI

Center for Environmental Measurements and Quality Assurance

March 31, 1992

Ms. Joan W. Etheridge
OWMC Laboratory
845 Harrington Court
Burlington, Ontario L7N3P3

Laboratory I.D. No.:
Digestion Methods: NIOSH 7082 and EPA/AREAL
Analytical Method: ICP

Dear Ms. Etheridge:

Thank you for your willingness to participate in a round robin analysis for lead in paint and dust supportive to the U.S. Environmental Protection Agency.

The round is designed to evaluate the level of lead in, and the homogeneity of, a group of performance evaluation samples for lead in paint and dust. A total of 35 laboratories will be participating in the round. Seven laboratories will be analyzing by laboratory XRF, and the remaining labs will be analyzing by AAS or ICP. Two of the participating labs will analyze the samples using both laboratory XRF and AAS/ICP. Your laboratory identification number and method of digestion [NIOSH 7082 (hotplate) or EPA/AREAL (microwave)] and analysis (AAS or ICP) selected by your laboratory is shown at the top of this letter and on the enclosed data reporting form.

Please find enclosed five (5) bottles of paint (P-1 through P-5), and five (5) bottles of dust samples (D-1 through D-5) for analysis. Upon receipt of the samples, please rotate the bottles gently through all axes for a couple of minutes in order to compensate for any separation that may have occurred during shipment.

At the time of sampling, please remove two aliquots from each sample and digest and analyze each aliquot separately. The enclosed data reporting form provides a blank for reporting the concentration of Aliquot 1 and Aliquot 2 for each sample, for a total of twenty (20) results for the analysis of the paint and dust materials. It is recommended that samples analyzed by ICP be diluted to a final solution concentration of less than 10 ppm.

Post Office Box 12194 Research Triangle Park, North Carolina 27709-2194
Telephone 919 541-6914 Fax: 919 541-5929

Protocols for preparation and analysis of samples are given in the report, "Standard Operating Procedures for Lead in Paint by Hotplate- or Microwave-based Acid Digestions and Atomic Absorption or Inductively Coupled Plasma Emission Spectrometry," already mailed to you under separate cover. Centrifuge tubes are required for the EPA/AREAL digestion method, and are enclosed. These tubes are not clean, and will need to be cleaned per the method described in the SOP report. Please follow the protocol given to clean the centrifuge tubes (EPA/AREAL digestion method), to carry out the digestion and to analyze samples.

An ICP Instrument Parameter Sheet is enclosed. Please complete it, along with the data reporting form, and send results to RTI no later than Thursday, April 30, 1992. The forms should be submitted to:

EPA/RTI Round Robin for Lead in Paint and Dust
Center for Environmental Measurements and Quality Assurance
Research Triangle Institute
P.O. Box 12194
Research Triangle Park, NC 27709

Attn: Emily Williams
Building 7

A statistical analysis and report of the round will be sent to participating laboratories by the end of June.

Again, thank you for your participation. If you have questions, please call either David Binstock or Emily Williams at (919) 541-6896 or (919) 541-6217, respectively.

Sincerely,

David Binstock

Emily Williams

ICP PARAMETER SHEET

Instrument _____
(Manufacturer/Model)

Nebulizer _____

Wavelength _____

Grating _____

Resolution _____

Focal Length _____

Background Correction _____

Interference Correction _____

Forward Power _____

Reflected Power _____

Plasma Frequency _____

Auxilliary Gas Flow Rate _____

Sample Introduction Rate _____

Calibration Standards and Calibration Check Samples _____

_____

_____

_____

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. _____

Digestion Method NIOSH 7082 Laboratory OWMC

Experience with this Method _____ years Laboratory

Analysis Method ICP Approval Signature:

Experience with this Method _____ years _____

Sample ID No.	Gross Concentration of Lead (ppm) Aliquot 1	Aliquot 2
P-1		
P-2		
P-3		
P-4		
P-5		
D-1		
D-2		
D-3		
D-4		
D-5		
Reagent Blank		

Appendix D-2

Letter of Instructions to Laboratory XRF Laboratories

RESEARCH TRIANGLE INSTITUTE

Center for Environmental Measurements and Quality Assurance

March 31, 1992

Ms. Phyllis Madigan
Massachusetts State Laboratory Institute
Environmental Lead Laboratory
Room 311
3305 South Street
Jamaica Plain, MA 02130

Laboratory I.D. No.:
Analytical Method: Laboratory XRF
Dear Ms. Madigan:

Thank you for your willingness to participate in a round robin analysis for lead in paint and dust supportive to the U.S. Environmental Protection Agency.

The round is designed to evaluate the level of lead in, and homogeneity of, a group of performance evaluation samples of paint and dust. A total of 35 laboratories will be participating in the round. Seven laboratories will be analyzing by laboratory XRF, and the remaining labs will be analyzing by AAS or ICP. Two of the participating labs will analyze the samples using both laboratory XRF and AAS/ICP. Your laboratory identification number is shown at the top of this letter and on the enclosed data reporting form.

Please find enclosed five (5) bottles of paint (P-1 through P-5), five (5) bottles of dust samples (D-1 through D-5), and two bottles of Dust Reference Materials, CIN 1 (2275 ppm), and BAL 1 (58 ppm). Upon receipt of the samples, and before sampling, please rotate the bottles gently through all axes for a couple of minutes in order to compensate for any separation that may have occurred during shipment.

At the time of analysis, please remove two aliquots from each bottle, prepare the aliquots as individual samples and analyze each. The enclosed data reporting form provides a place for reporting the concentration of Aliquot 1 and Aliquot 2 for each sample, for a total of twenty (20) results if your lab is participating in the analysis of both paint and dust.

Post Office Box 12194 Research Triangle Park, North Carolina 27709-2194
Telephone 919 541-6914 Fax: 919 541-5929

We are requesting that laboratories follow their own protocol for the XRF analysis. Please use an amount of material that corresponds to an infinitely thick sample relative to the excitation beam, and run the sample in a cup that is approximately 31 mm in diameter. Otherwise, please select parameters that optimize your laboratory operations, and enter these parameters on the enclosed XRF parameter form. Laboratories using a wavelength-dispersive instrument, rather than an energy-dispersive instrument, are asked to contact RTI before the analyses are begun. As a reference, a protocol from the EPA 3-City Study will be mailed to you under separate cover at a later date.

When analyzing the paint samples, please calibrate the instrument with the standards routinely used in your operations. For the dust samples, we are requesting that you calibrate with the two reference materials enclosed (BAL 1 and CIN 1). If you have your own dust standards, please run your standards as samples relative to the calibration curve generated with CIN 1 and BAL 1; and report the values for your standards on the enclosed XRF Parameter Sheet for Dust.

Please use the enclosed data reporting form to submit results to RTI no later than Thursday, April 30, 1992. The XRF parameter form and data reporting form should be submitted to:

EPA/RTI Round Robin for Lead in Paint and Dust
Center for Environmental Measurements and Quality Assurance
Research Triangle Institute
P.O. Box 12194
Research Triangle Park, NC 27709

Attn: Emily Williams
Building 7.

A statistical analysis and report of the round will be sent to participating laboratories by the end of July.

Again, thank you for your participation. If you have questions, please call me at (919) 541-6217.

Sincerely,

Emily Williams

Emily Williams

LABORATORY XRF PARAMETERS - PAINT

Sample Quantity_____

Sample Preparation

_____

_____

_____

_____

_____

_____

Instrument_____

Description of X-ray Source_____

_____

Description of Secondary Target_____

_____

Description of Detector_____

_____

Reference_____

LABORATORY XRF PARAMETERS - PAINT

Counting Time _____

Counting Rate _____

Total Counts _____

Calibration Standards _____

_____

_____

Results of Calibration Check Samples _____

_____

_____

_____

LABORATORY XRF PARAMETERS - DUST

Sample Quantity _____

Sample Preparation

_____

_____

_____

_____

_____

_____

Instrument _____

Description of X-ray Source _____

_____

Description of Secondary Target _____

_____

Description of Detector _____

_____

Reference _____

LABORATORY XRF PARAMETERS - DUST

Counting Time_____

Counting Rate_____

Total Counts_____

Calibration Standards -- CIN 1 and BAL 1

Results of Calibration Check Samples_____

_____

_____

_____

EPA/RTI Round Robin for Lead In Paint and Dust

Round Robin No. 002 Lab ID No. _____

Digestion Method N/A Laboratory MA State

Experience with this Method _____ years Laboratory Institute

Analysis Method Lab XRF Approval Signature:

Experience with this Method _____ years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1		
P-2		
P-3		
P-4		
P-5		
D-1		
D-2		
D-3		
D-4		
D-5		
Reagent Blank	N/A	
	N/A	
	N/A	
	N/A	

Appendix D-3

RTI Copy of Data Reporting Form with Sequence Tracking

EPA/RTI Round Robin for Lead In Paint and Dust

Round Robin No. 002 Lab ID No. _____

Digestion Method N/A Laboratory MA State

Experience with this Method _____ years Laboratory Institute

Analysis Method Lab XRF Approval Signature:

Experience with this Method _____ years _____

Sample ID No.	Gross Concentration of Lead (ppm) Aliquot 1	Aliquot 2
P-1 - 25		
P-2 - 25		
P-3 - 25		
P-4 - 25		
P-5 - 25		
D-1 - 25		
D-2 - 25		
D-3 - 25		
D-4 - 25		
D-5 - 25		
Reagent Blank	N/A	
	N/A	
BAL - 1 - 5	N/A	
CIN - 1 - 5	N/A	

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. _____

Digestion Method EPA/AREAL Laboratory WI Occupational

Experience with this Method _____ years Health Laboratory

Analysis Method ICP Approval Signature:

Experience with this Method _____ years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1 - 4		
P-2 - 4		
P-3 - 4		
P-4 - 4		
P-5 - 4		
D-1 - 4		
D-2 - 4		
D-3 - 4		
D-4 - 4		
D-5 - 4		
Reagent Blank		

EPA/RTI Round Robin for Lead In Paint and Dust

Round Robin No. 002 Lab ID No. _____

Digestion Method NIOSH 7082 Laboratory OMMC

Experience with this Method _____ years Laboratory

Analysis Method ICP Approval Signature:

Experience with this Method _____ years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1 -28		
P-2 -28		
P-3 -28		
P-4 -28		
P-5 -28		
D-1 -28		
D-2 -28		
D-3 -28		
D-4 -28		
D-5 -28		
Reagent Blank		

Appendix E

Reported Results

Appendix E-1

MW/AAS Laboratories

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 10

Digestion Method EPA/AREAL Laboratory _____

Experience with this Method < 1 years _____

Analysis Method AA Approval Signature/

Experience with this Method 10 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1500	1900
P-2	164,000	143,000
P-3	52,000	44,000
P-4	2300	2000
P-5	45,000	45,000
D-1	4800	5300
D-2 *	90	91
D-3	1100	1200
D-4 *	90	100
D-5	5100	5400

* Determined by Graphite Furnace AA. All others by Flame AA

Reagent Blank	
Digestion Blank	< 10 ppb
DI Water Blank	< 10 ppb

AAS INSTRUMENT PARAMETER SHEET

Instrument Flame AA - Perkin Elmer 603 / Graphite Furnace - Perkin Elmer 3[redacted]0
(Manufacturer/Model)

Wavelength/Slit Width 283.3 / 0.7 (Both systems)

Background Correction Deuterium Arc / Zeeman

Interference Correction None / GFAA: $Mg(NO_3)_2 \cdot 6H_2O$ and NH_4H_2P[redacted]

Light Source HC Lamp

Flame Type Acetylene / Air

Calibration Standards and Calibration Checks Flame System -- NIST SRM 3174 diluted to 25ppm. Recovery 105% (26.3ppm). GFAA - NIST 3174 diluted to 25ppb. Recovery 98.8% (24.7ppb).

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 11

Digestion Method EPA/AREAL Laboratory _____

Experience with this Method 0.5 years _____

Analysis Method AA Approval Signature:

Experience with this Method ~~0.5~~ 2.5 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1510	2010
P-2	110,200	117,300
P-3	34,600	40,800
P-4	2053	1640
P-5	37,600	41,900
D-1	4920	4340
D-2	115	117
D-3	1060	1140
D-4	116	103
D-5	4630	4500
Reagent Blank	< 3.0 µg	
	< 3.0 µg	

AAS INSTRUMENT PARAMETER SHEET

Instrument PERKIN ELMER 3030B
(Manufacturer/Model)

Wavelength/Slit Width 217.0 nm, 0.7 nm slit width

Background Correction NONE

Interference Correction Dual Beam, Continuum Source

Light Source PE single element Hollow Cathode Lamp

Flame Type Air-Acetylene/Oxidizing - Lean Blue

Calibration Standards and Calibration Checks

STANDARDS: (MG/L) 1.0, 2.0, 5.0, 10.0

CHECKS: REAGENT BLANK, 1.0 MG/L VERIFICATION, FULL CURVE VERIFIC
AND NBS 1579 PAINT CONTROL

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 12

Digestion Method EPA/AREAL Laboratory _____

Experience with this Method 1 years _____

Analysis Method AA Approval Signature:

Experience with this Method 4 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1801	1735
P-2	90520	106200
P-3	37700	39430
P-4	2165	2280
P-5	22440	22640
D-1	4155	4956
D-2	451	465
D-3	1648	1674
D-4	539	567
D-5	3929	4187
Reagent Blank	0.39	
	2.04	
	2.40	

AAS INSTRUMENT PARAMETER SHEET

Instrument PERKIN-ELMER 5100 PC
(Manufacturer/Model)

Wavelength/Slit Width 283.3 nm 0.7 slit (high)

Background Correction D2

Interference Correction none

Light Source Pb hollow cathode

Flame Type AIR/ACETYLENE

Calibration Standards and Calibration Checks 0, 1, 5, 10, 20 µg/mL Pb
from High Purity Standard® 1000 µg/mL Lot# 190422
Cal. checks at 5.0 µg/mL and 20.0 µg/mL.

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 13

Digestion Method EPA/AREAL Laboratory _____

Experience with this Method 0 years _____

Analysis Method AA Approval Signature:

Experience with this Method 15 years _____

Gross Concentration of Lead (~~ppm~~) (µg/g)

Sample ID No.	Aliquot 1	Aliquot 2
P-1	1810	1810
P-2	114000	116000
P-3	40500	41800
P-4	1880	2010
P-5	43300	46300
D-1	4870	5130
D-2	99	98
D-3	1440	1490
D-4	128	98
D-5	5190	5580

Reagent Blank < 0.2 µg/mL

Method Blank spiked with 10 µg/mL prior to digestion was 104.7% of true value

AAS INSTRUMENT PARAMETER SHEET

Instrument GBC Model
(Manufacturer/Model)

Wavelength/Slit Width 283.3 nm

Background Correction None

Interference Correction None

Light Source Hollow cathode, Pb single element

Flame Type C_2H_2 - Air

Calibration Standards and Calibration Checks 0, 1, 5, 10, 20 ug/mL in 1% HNO_3; ICV = 10 ug/mL, CCVs = 10 ug/mL Calibration coeff = 0.9994, all other calibration checks within ± 10% of true value.

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 14

Digestion Method EPA/AREAL Laboratory _____

Experience with this Method _____ years _____

Analysis Method AA Approval Signature:

Experience with this Method _____ years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1773	1669
P-2	109414	127416
P-3	38312	36048
P-4	1576	1522
P-5	35498	36621
D-1	5022	4210
D-2	196	177
D-3	1292	1277
D-4	97	87
D-5	4797	4686
Reagent Blank	0	

AAS INSTRUMENT PARAMETER SHEET

NIOSH 7082

Instrument Perkin Elmer 603
(Manufacturer/Model)

Wavelength/Slit Width 283.3/4

Background Correction

Interference Correction

Light Source Hollow Cathode (lamp # 252531)

Flame Type lean Air- C_2H_2

Calibration Standards and Calibration Checks

Standards: 0.5, 1, 2, 5, 10, 20, 40 ppm

Calibration checks: One of the above after every 6th sample

Standards/Samples plotted on linear square calibration curve.

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 15

Digestion Method EPA/AREAL Laboratory _____

Experience with this Method 0 years _____

(Experience with Microwave Digest'n 2.5 years.)

Analysis Method AA Approval Signature:

Experience with this Method 4.5 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	2130.	2250.
P-2	130,000.	129,000.
P-3	43700.	42300.
P-4	2370.	1960.
P-5	41600.	40200.
D-1	4920.	5450.
D-2	99.	105.
D-3	1280.	1300.
D-4	168.	97.
D-5	5180.	4970.
Reagent Blank	00.0	
	00.0	

AAS INSTRUMENT PARAMETER SHEET

Instrument Varian SpectrAA 400
(Manufacturer/Model)

Wavelength/Slit Width 217.0 nm / 1.0 nm

Background Correction Deuterium Lamp

Interference Correction none

Light Source Varian Hollow Cathode lamp for Pb.

Flame Type Air-Acetylene

Calibration Standards and Calibration Checks Calibration standards made from Aldrich® Pb AA stnd. solution, 1020 ppm Pb. Calibration check samples were standards made from NIST stock standard solution.

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 16

Digestion Method EPA/AREAL Laboratory _____

Experience with this Method 0 years _____

Analysis Method AA Approval Signature:

Experience with this Method 22 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1,920	1,720
P-2	131,000	126,000
P-3	41,500	41,300
P-4	2,050	1,740
P-5	42,700	43,600
D-1	4,720.	4,930.
D-2	130.	130.
D-3	1,340	1,340.
D-4	140	140
D-5	4,800.	5,040

Reagent Blank

0.00 µg/ml

0.00 µg/ml

AAS INSTRUMENT PARAMETER SHEET

Instrument Perkin-Elmer Model 5000 AAS
(Manufacturer/Model)

Wavelength/Slit Width 283.3 nm / 0.7 nm

Background Correction

Interference Correction

Light Source Perkin-Elmer Intensitron hollow cathode lamp

Flame Type air-acetylene, oxidizing

Calibration Standards and Calibration Checks 2, 5, 10, and 20 ug Pb/ml

Appendix E-2

HP/AAS Laboratories

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 20

Digestion Method NIOSH 7082 Laboratory _____

Experience with this Method 2 years _____

Analysis Method AA Approval Signature:

Experience with this Method _____ years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1350	1213
P-2	105667	110000
P-3	33833	36098
P-4	1383	1478
P-5	32055	35567
D-1	3531	4463
D-2	89	84
D-3	1208	1177
D-4	65	79
D-5	3191	4196
Reagent Blank	<50	
	<50	

AAS INSTRUMENT PARAMETER SHEET

Instrument Thermo Jarrell Ash Video 22
(Manufacturer/Model)

Wavelength/Slit Width 283.3 / 0.7

Background Correction Deuterium

Interference Correction —

Light Source LEAD Hollow Cathode

Flame Type Air / Acetylene

Calibration Standards and Calibration Checks Stds: Fisher (02, 05, 10, 20 ppm); Checks: SPEX (02, 10 ppm) Std. Reference Material NIST 1579

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 21

Digestion Method NIOSH 7082 Laboratory _____

Experience with this Method 20 years _____

Analysis Method AA Approval Signature:

Experience with this Method 20 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1790	1700
P-2	140,000	132,000
P-3	41,000	39,500
P-4	2030	1990
P-5	43,600	46,300
D-1	5300	5740
D-2	116	98
D-3	1260	1290
D-4	130	100
D-5	4990	5280
Reagent Blank	0.7 µg	
	1.0 µg	
	1.1 µg	

AAS INSTRUMENT PARAMETER SHEET

Instrument IL Model 251
(Manufacturer/Model)

Wavelength/Slit Width 217.0 320μ

Background Correction NO

Interference Correction

Light Source HOLLOW CATHODE LAMP - Pb

Flame Type AIA - ACETYLENE

Calibration Standards and Calibration Checks AQUEOUS STD,
EPA QC Material, NBS 1579 PAINT STD

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 22

Digestion Method NIOSH 7082 Laboratory _____

Experience with this Method 210 years _____

Analysis Method AA Approval Signature:

Experience with this Method 210 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1696	1324
P-2	118820	115359
P-3	34991	33550
P-4	1146	1080
P-5	35010	34140
D-1	4840	4709
D-2	97	100
D-3	960	960
D-4	92	96
D-5	4694	4520
Reagent Blank	0.00	
	0.00	
	0.00	

AAS INSTRUMENT PARAMETER SHEET

Instrument Thermo Jarrell Ash Video 22
(Manufacturer/Model)

Wavelength/Slit Width 1.0

Background Correction 1.5 Signal 3.0

Interference Correction

Light Source Thermo Jarrel Ash Visimax II Hollow Cathode Lamp

Flame Type air-acetylene

Calibration Standards and Calibration Checks

Standards: 0.50, 1.00, 2.00, and 5.00 µg/mL

Quality Controls: 0.67 µg/mL

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 23

Digestion Method NIOSH 7082 Laboratory _____

Experience with this Method 1 years _____

Analysis Method AA Approval Signature:

Experience with this Method 1 years _____

		Gross Concentration of Lead (ppm)	
Sample ID No.		Aliquot 1	Aliquot 2
P-1	1,544	~~1500~~ KLH mg/kg	~~1400~~ KLH mg/kg 1438
P-2	116,025	~~100,000~~ KLH mg/kg	~~10,000~~ KLH mg/kg 99,577
P-3	36,790	~~37,000~~ KLH mg/kg	~~43,000~~ KLH mg/kg 42,605
P-4	1,446	~~1400~~ KLH mg/kg	~~1500~~ KLH mg/kg 1,458
P-5	37,144	~~37,000~~ KLH mg/kg	~~30,000~~ KLH mg/kg 35,990
D-1	4,464	~~4500~~ KLH mg/kg	~~4500~~ KLH mg/kg 4504
D-2		96 mg/kg	100 mg/kg
D-3	1,067	~~1400~~ KLH mg/kg	~~1400~~ KLH mg/kg 1,113
D-4		~~100~~ 110 mg/kg MTS 5-16-92	~~100~~ 110 mg/kg MTS 5-16-92
D-5	4,333	~~4300~~ KLH mg/kg	~~4700~~ KLH mg/kg 4,669
Reagent Blank		<0.50	

AAS INSTRUMENT PARAMETER SHEET

Instrument PERKIN ELMER 3100 ATOMIC ABSORPTION SPECTROMETER
(Manufacturer/Model)

Wavelength/Slit Width 283.3 / 0.7 HIGH

Background Correction —

Interference Correction —

Light Source

Flame Type AIR / ACETYLENE

Calibration Standards and Calibration Checks

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 24

Digestion Method NIOSH 7082 Laboratory _____

Experience with this Method 5 years _____

Analysis Method AA Approval Signature:

Lab Experience with this Method 18 years _____

Analyst experience 3 years

Sample ID No:	Gross Concentration of Lead (ppm) Aliquot 1	Aliquot 2
✓ P-1	1510	1,790
✓ P-2	102,000	111,000
✓ P-3	33,500	39,500
✓ P-4	1,940	1,790
✓ P-5	36,900	41,600
✓ D-1	3,990	4,390
✓ D-2	< 100	140
✓ D-3	1,130	1,240
✓ D-4	108	171
✓ D-5	4603	5,710
Reagent Blank	< 100	
	< 100	

AAS INSTRUMENT PARAMETER SHEET

Instrument PERKIN ELMER 3030
(Manufacturer/Model)

Wavelength/Slit Width 217.0 ~~0~~ 0.7

Background Correction ~~N/A~~ DEUTERIUM LAMP

Interference Correction N/A

Light Source HOLLOW CATHODE LAMP

Flame Type AIR / ACETYLENE

Calibration Standards and Calibration Checks 0 ppm, 1 ppm, 5 ppm, 10 ppm, 20 ppm

CALIBRATION CHECK WAS WITH 3.0 ppm STD.

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 25

Digestion Method NIOSH 7082 Laboratory _____

Experience with this Method 6 years _____

Analysis Method AA Approval Signature:

Experience with this Method 10 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1310	2064
P-2	14010	5077
P-3	36594	35340
P-4	1852	2047
P-5	34614	35772
D-1	4143	3889
D-2	214	199
D-3	1186	1217
D-4	85	93
D-5	5241	5179
Reagent Blank	0	
	0	
	0	
	0	

AAS INSTRUMENT PARAMETER SHEET

Instrument Perkin Elmer Atomic Absorption Spectrometer 31[redacted]
(Manufacturer/Model)

Wavelength/Slit Width D: 217nm 0.7

Background Correction Deuterium

Interference Correction none

Light Source Hollow Cathode Lamp

Flame Type Air Acetylene

Calibration Standards and Calibration Checks Calib. stds, 1, 2, 4, 6, 8, 10ppm

Calib. check 5ppm

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 26

Digestion Method NIOSH 7082 Laboratory _____

Experience with this Method 1 years _____

Analysis Method AA Approval Signature:

Experience with this Method 28 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1700	1600
P-2	46,000	55000
P-3	36,000	35,000
P-4	1700	1800
P-5	36,000	37,000
D-1	4700	4700
D-2	143	120
D-3	1200	1200
D-4	110	130
D-5	4800	4700
Reagent Blank	< 1.0 µg	

AAS INSTRUMENT PARAMETER SHEET

Instrument Perkin Elmer 2100 - AAS
(Manufacturer/Model)

Wavelength/Slit Width 217.1nm. / 0.7 nm

Background Correction None

Interference Correction None

Light Source Lead Hollow Cathode Tube Lamp

Flame Type Air - Acetylene

Calibration Standards and Calibration Checks Standards of 2 and 10 ppm were used to calibrate the instrument. Samples were read in triplicate & the calibration was checked every 5 samples. One spiked sample was made for every 10 samples and a QC metals composite solution was also checked.

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 27

Digestion Method NIOSH 7082 Laboratory _____

Experience with this Method _____ years _____

Analysis Method AA Approval Signature:

Experience with this Method 0 years _____
(13 years experience with AA method)

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1542	2096
P-2	93,532	99,463
P-3	37,699	35,974
P-4	1,805	1,879
P-5	37160	37002
D-1	4567	5014
D-2	109	111
D-3	1199	1207
D-4	109	140
D-5	5096	4071
Reagent Blank	0	

AAS INSTRUMENT PARAMETER SHEET
NIOSH 7082

Instrument Perkin Elmer 603
(Manufacturer/Model)

Wavelength/Slit Width 283.3/4

Background Correction

Interference Correction

Light Source Hollow Cathode (lamp # 252531)

Flame Type lean Air- C2H2

Calibration Standards and Calibration Checks

Standards: 0.5, 1, 2, 5, 10, 20, 40 ppm

Calibration checks: One of the above after every 6th sample

Standards/Samples plotted on linear square calibration curve.

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 28

Digestion Method NIOSH 7082 Laboratory _____

Experience with this Method 1 years _____

Analysis Method AA Approval Signature:

Experience with this Method 22 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	2020	1640
P-2	112,000 ~~11,200~~	113,000 ~~11,300~~
P-3	39,000	38,400
P-4	1760	1900
P-5	38,700	38,600
D-1	4680	4150
D-2	< 300	< 300
D-3	1180	1320
D-4	< 300	< 300
D-5	5080	4760
Reagent Blank	0.00 µg/ml	
	0.00 µg/ml	

AAS INSTRUMENT PARAMETER SHEET

Instrument Perkin Elmer Model 5000 AAS
(Manufacturer/Model)

Wavelength/Slit Width 283.3 nm / 0.7 nm

Background Correction

Interference Correction

Light Source Perkin-Elmer Intensitron hollow cathode lamp

Flame Type air-acetylene, oxidizing

Calibration Standards and Calibration Checks 2, 5, 10, and 20 µg Pb/ml

Appendix E-3

MW/ICP Laboratories

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 30

Digestion Method EPA/ALEAL Laboratory _____

Experience with this Method 0 years _____

Analysis Method ICP Approval Signature:

Experience with this Method 5 years _____

Sample ID No.	Gross Concentration of Lead (ppm) Aliquot 1	Aliquot 2
P-1	1640.	< 9.8
P-2	112000.	99200.
P-3	36100.	35600.
P-4	1490.	1980.
P-5	35400.	25000.
D-1	3980.	4620.
D-2	90.	85.
D-3	1010.	1180.
D-4	125.	100.
D-5	3500.	5010.
Reagent Blank	< 50 µg/l	
	< 50 µg/l	

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 31

Digestion Method EPA/AREAL Laboratory _____

Experience with this Method 3 years _____

Analysis Method ICP Approval Signature:

Experience with this Method 3 years _____

	Gross Concentration of Lead (ppm) = mg/g	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1670	1,220
P-2	135,000	123,000
P-3	37,800	38,000
P-4	1,230	1,490
P-5	35,800	38,700
D-1	3,090	3,690
D-2	87.0	108
D-3	1,010	1060
D-4	97.4	84.2
D-5	3480	3840
Reagent Blank	ND < 0.09 mg/L	
	ND < 0.09	
	ND < 0.09	
	ND < 0.09	

ICP PARAMETER SHEET

Instrument Leeman PS 2000
(Manufacturer/Model)

Nebulizer Hildebrand Grid

Wavelength 220.35

Grating Echelle

Resolution 0.0075 nm

Focal Length 1.0 meter

Background Correction Yes

Interference Correction Yes

Forward Power 1.0 kW

Reflected Power (Because of Seeman design, which uses a "running" oscillator, there is no reflected power.)

Plasma Frequency 40.68 MHz

Auxilliary Gas Flow Rate 0 L/min

Sample Introduction Rate 1.3 ml/min

Calibration Standards and Calibration Check Samples

Calibration Stds 10 ppm + Blank

Update Stds 5 ppm + Blank

Continuing Calibration Std 1.0 ppm

QC Check Std (Separate Source) 1.0 ppm

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 32

Digestion Method EPA/AREAL Laboratory _____

Experience with this Method 0 years _____

Analysis Method ICP Approval Signature:

Experience with this Method 7 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1410	1750
P-2	116000	118000
P-3	34400	33800
P-4	1370	1600
P-5	35500	35400
D-1	3740	4230
D-2	107	97.5
D-3	1200	1150
D-4	88.4	103
D-5	3460	4680
Reagent Blank	PAINT ND 10.0	
	DUST ND 10.0	

ICP PARAMETER SHEET

Instrument Thermo Jarrell-Ash 61E Purge
(Manufacturer/Model)

Nebulizer Fixed cross-Flow

Wavelength 220.353 nm

Grating Diffraction Grating 2400 Grooves/mm

Resolution 0.53nm/mm

Focal Length 0.75 meters

Background Correction Low offset -14

Interference Correction Al, Cr, Fe, Ti

Forward Power 950 W

Reflected Power No Meter Available

Plasma Frequency 27.12 MHz

Auxilliary Gas Flow Rate 0.2 L/M.n

Sample Introduction Rate 1.5 ml/M.n

Calibration Standards and Calibration Check Samples ITAS1 - Blank

ITAS #4 Pb=10ppm ICV-1 (EPA 0691) Pb = 5.203 ppm

CCV1 Pb = 2ppm

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 33

Digestion Method EPA/AREAL Laboratory _____

Experience with this Method 4 years _____

Analysis Method ICP Approval Signature:

Experience with this Method 3 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1432.	1408.
P-2	109400.	109600.
P-3	34000.	34100.
P-4	1518.	1502.
P-5	32400.	32600.
D-1	4160.	4170.
D-2	87.	89.
D-3	1142.	1104.
D-4	145.	98.
D-5	3960.	3960.
Reagent Blank	< 10.	

ICP PARAMETER SHEET

Instrument Leeman Labs Inc.; ICP/PS 1000
(Manufacturer/Model)

Nebulizer 42 PSI

Wavelength 220.353

Grating Fixed Echelle Grating

Resolution

Focal Length

Background Correction 220.330

Interference Correction Inter Element Correction for Aluminum

Forward Power 1.1 kW

Reflected Power

Plasma Frequency 40.68 mHz

Auxilliary Gas Flow Rate .00 LPM

Sample Introduction Rate 1.7 ml/min

Calibration Standards and Calibration Check Samples

Calibration Standards: 0.0, 0.5, 3.0, 10.0, 30.0, and 100.0 PPM

Calibration Check Standards: 0.0, 2.0 and 100.0 PPM +/- 10 %

run after every 10 samples.

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 34

Digestion Method EPA/AREAL Laboratory _____

Experience with this Method _____ years _____

Analysis Method ICP Approval Signature:

Experience with this Method 6 years _____

Sample ID No.	Gross Concentration of Lead (ppm) Aliquot 1	Aliquot 2
P-1	1,500 ppm	1,880 ppm
P-2	117,000 ppm	120,000 ppm
P-3	35,200 ppm	36,700 ppm
P-4	1,550 ppm	1,830 ppm
P-5	33,700 ppm	35,200 ppm
D-1	4,070 ppm	4,960 ppm
D-2	80 ppm	140 ppm
D-3	1,170 ppm	1,180 ppm
D-4	170 ppm	110 ppm
D-5	4,110 ppm	3,900 ppm
Reagent Blank	<1 ug/sample	

ICP PARAMETER SHEET

Instrument Jarrell-Ash 9000 Air Spectrometer
(Manufacturer/Model)

Nebulizer Fixed Cross Flow

Wavelength 2203.00

Grating 1516 groves/mm ruled grating at 500 nm

Resolution .045 nm, First Order, .023 nm, Second Order, .015 nm Third [redacted]

Focal Length Focal curve is 580 mm in length

Background Correction No

Interference Correction Yes Fe, Mg, Al

Forward Power 1.2 Kilometer

Reflected Power 0

Plasma Frequency

Auxilliary Gas Flow Rate 22 LPM

Sample Introduction Rate 2.7 ml per min

Calibration Standards and Calibration Check Samples

Fisher Lead Reference Solution 1,000 ppm ± 1%

NIST Reference Std QC 3469	Lead Reported 58.2 ug/f Actual 56.9 ug/f
NIST Reference Std QC 34370	Lead Reported 40 ug/f Actual 37.8 ug/f

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 35

Digestion Method EPA/AREAL Laboratory _____

Experience with this Method _____ years _____

Analysis Method ICP Approval Signature:

Experience with this Method _____ years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1540	1680
P-2	119000	123000
P-3	38900	37600
P-4	1400	1410
P-5	36600	41000
D-1	5640	4840
D-2	74	83
D-3	950	1070
D-4	72	84
D-5	4270	4190
Reagent Blank	< 2 (mg/kg)	
	< 2	
	< 2	
	< 2	

ICP PARAMETER SHEET

Instrument Thermo Jarrell Ash 61
(Manufacturer/Model)

Nebulizer fixed cross flow

Wavelength 2203.53 (X 2)

Grating holographic 2700 lines/mm

Resolution

Focal Length 3/4 M

Background Correction yes

Interference Correction yes

Forward Power 1.1 KW

Reflected Power <10 W

Plasma Frequency 27.12

Auxilliary Gas Flow Rate 0

Sample Introduction Rate 1.1 ml/min

Calibration Standards and Calibration Check Samples yes

BLANK + 1PPM - CALIBRATION

1PPM - CHECK

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 36

Digestion Method EPA/AREAL Laboratory _____

Experience with this Method 1 MON ~~years~~ _____

Analysis Method ICP Approval Signature: _____

Experience with this Method 7 years _____

Sample ID No.	Gross Concentration of Lead (ppm) Aliquot 1	Aliquot 2
P-1	1600	1400
P-2	116,000	115,000
P-3	35,800	35,000
P-4	2120	1590
P-5	39,400	37,600
D-1	4260	3940
D-2	126	98
D-3	1220	1150
D-4	88	98
D-5	4720	5360
Reagent Blank	0	
	0	

ICP PARAMETER SHEET

Instrument: Perkin Elmer 6000 ICP
(Manufacturer/Model)

Nebulizer: Cross Flow

Wavelength: 220. 353 nm

Grating: UV grating – holographic

Resolution: 0.001 nm

Focal Length: 408 mm

Background Correction: Yes

Interference Correction: Yes

Forward Power: 1.20 Kilowatts

Reflected Power: Less than 5 watts

Plasma Frequency: 27.12 MHz ISM Band

Auxilliary Gas Flow Rate: 0.6 L/min

Sample Introduction Rate: 1.1 mL/min

Calibration Standards and Calibration Check Samples

1. Calibration standards – 0.00 and 10.00 µg/mL
2. Check samples – 0.00 and 10.00 µg/mL
3. The 0.00 µg/mL check sample could not drift beyond ±0.05 ug/mL and the 10.00 µg/mL sample beyond 5% (9.50 and 10.50 µg/mL).
4. A manually plotted line using 0.00, 0.50, 3.00, and 10.00 µg/mL standards resulted in an r square value of 1.000.

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 37

Digestion Method EPA/AREAL Laboratory _____

Experience with this Method 0 years _____
3 YEARS EXPERIENCE WITH MICROWAVE METHODS

Analysis Method ICP Approval Signature:

Experience with this Method 8 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1896	1529
P-2	126637	120216
P-3	42112	37519
P-4	1995	1775
P-5	37685	37270
D-1	4980	4443
D-2	211	101
D-3	1192	1206
D-4	98.9	97.6
D-5	4258	4026
Reagent Blank	< 10	
	< 10	
	< 10	
	< 10	

ICP PARAMETER SHEET

Instrument ARL 3560
(Manufacturer/Model)

Nebulizer MEINHARD - 45PSI 1.2 LPM ARGON FLOW

Wavelength 220.35nm Pb 3RD ORDER; 267.72nm Cr 3RD ORDER

Grating 1080 GROOVES/mm MECHANICAL

Resolution FWHM 0.016nm IN 3RD ORDER; 0.93nm/mm 1ST ORDER RLD

Focal Length 1 METER F17

Background Correction ± 0.25nm

Interference Correction
200 PPM Ti = 0.1153 PPm FALSE Pb
500 PPM Cr = 0.0233 PPm FALSE Pb
500 PPM Al = 0.0685 PPm FALSE Pb
} CORRECTION AUTOMATICALLY APPLIED

Forward Power 650 WATTS (MINITORCH @ 8 LPm COOLANT ARGON)

Reflected Power < 10 WATTS

Plasma Frequency 27.12 MHz

Auxilliary Gas Flow Rate 0

Sample Introduction Rate 1.0 ml/min

Calibration Standards and Calibration Check Samples BLANK, 0.5, 3, 10, 30, 100 PPm OF Pb, Cr (SOURCE = SPEX) INITIAL CALIBRATION CHECK = ICV-1, ICV-4 (SOURCE = EPA) CONTINUING CALIBRATION CHECK = 5 PPm (SOURCE = INORGANIC VENTURES)

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 38

Digestion Method EPA/AREAL Laboratory _____

Experience with this Method 0 years _____

Analysis Method ICP Approval Signature:

Experience with this Method 8 years _____ _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	DIGESTION TUBE MELTED	1700
P-2	120000	130000
P-3	39000	38000
P-4	1600	1800
P-5	39000	40000
D-1	4800	4300
D-2	<22	<22
D-3	1200	1200
D-4	100	31
D-5	4700	2500
Reagent Blank	Below detection limit for this wavelength which is 0.05 mg/L	

ICP PARAMETER SHEET

Instrument ARL 3510
(Manufacturer/Model)

Nebulizer Meinhard

Wavelength 220.353 nm

Grating 2400 groves/mm, Holographic

Resolution 0.0112 nm (Information from Factory Test)

Focal Length 1 meter

Background Correction Two point background correction

Interference Correction many - but results checked at two other lead wavelengths, 293.3 and 405.7 nm.

Forward Power 1200

Reflected Power 1

Plasma Frequency 27.12 MHz.

Auxilliary Gas Flow Rate 30 psi for coolant gas
18 psi for plasma gas

Sample Introduction Rate ~1 mL/min

Calibration Standards and Calibration Check Samples standards at 0, 10, 20, and 100 mg/L lead

Appendix E-4

HP/ICP Laboratories

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 40

Digestion Method NIOSH 7082 Laboratory _____

Experience with this Method 0 years _____

Analysis Method ICP Approval Signature:

Experience with this Method 5 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1650.	2330.
P-2	78700.	115000.
P-3	34500.	42200.
P-4	1840.	2010.
P-5	34100.	38700.
D-1	3860.	5750.
D-2	98.	54.
D-3	1010.	1530.
D-4	90.	48.
D-5	5860.	7150.
Reagent Blank	< 50 µg/l	
	< 50 µg/l	

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 41

Digestion Method NIOSH 7082 Laboratory: _____

Experience with this Method 2 years _____

Analysis Method ICP Approval Signature:

Experience with this Method 3 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1 06611	1.757	1.685
P-2 06612	114.76	111.62
P-3 06613	47.30	36.54
P-4 06614	1.872	1.607
P-5 06615	41.26	44.34
D-1 06616	3.365	5.033
D-2 06617	0.150	0.142
D-3 06618	1.317	1.241
D-4 06619	<0.100	<0.100
D-5 06620	5.538	5.112
Reagent Blank	<0.100	
	<0.100	
	<0.100	
	<0.100	

These results were rechecked by the analyst and found to be incorrect by three orders of magnitude. The above results were multiplied by 1000 and entered into the database.

ICP PARAMETER SHEET

Instrument ARL (Applied Research Laboratories) ICP/Model 3410
(Manufacturer/Model)

Nebulizer Meinhard

Wavelength 220.353

Grating Ruled

Resolution 2400 lines/inch

Focal Length 1 meter spectrophotometer

Background Correction Not necessary

Interference Correction Not necessary

Forward Power 671 Watts

Reflected Power 001 Watts.

Plasma Frequency 25 megaHertz

Auxilliary Gas Flow Rate Coolant = 7.5 L/min, Plasma = 0.30 L/min.

Sample Introduction Rate 2.5 mL/minute

Calibration Standards and Calibration Check Samples

1. Initially I analysed each sample with controls & standards which bracketed the sample concentration.

2. I analysed using BLANK, 1 ppm, 3 ppm, 10 ppm, Control = 5 ppm. and diluted samples if necessary to fall within these standards.

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 42

Digestion Method NIOSH 7082 Laboratory _____

Experience with this Method 4 years _____

Analysis Method ICP Approval Signature:

Experience with this Method 3 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1790.	1615.
P-2	119000.	115000.
P-3	34500.	34700.
P-4	1450.	1630.
P-5	34500.	34100.
D-1	4060.	4460.
D-2	93.	108.
D-3	1120.	1100.
D-4	74.	90.
D-5	4220.	4110.
Reagent Blank	< 50.	

ICP PARAMETER SHEET

Instrument Leeman Labs Inc.; ICP/PS 1000
(Manufacturer/Model)

Nebulizer 42 PSI

Wavelength 220.353

Grating Fixed Echelle Grating

Resolution

Focal Length

Background Correction 220.330

Interference Correction Inter Element Correction for Aluminum

Forward Power 1.1 kW

Reflected Power

Plasma Frequency 40.68 mHz

Auxilliary Gas Flow Rate .00 LPM

Sample Introduction Rate 1.7 ml/min

Calibration Standards and Calibration Check Samples

Calibration Standards: 0.0; 0.5; 3.0; 10.0; 30.0; and 100.0 PPM

Calibration Check Standards: 0.0; 2.0; and 100.0 PPM +/- 10 %

run after every 10 samples.

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 43

Digestion Method NIOSH 7082 Laboratory: _____

Experience with this Method 3 years _____

Analysis Method ICP Approval Signature:

Experience with this Method 11 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1,556	1,537
P-2	110,500	113,400
P-3	37,140	35,870
P-4	1,882	1,744
P-5	36,510	36,980
D-1	4,013	4,414
D-2	102	100
D-3	1,249	1,220
D-4	104	97.3
D-5	4,535	4,532
Reagent Blank	−0.01	
	−0.02	
	+0.02	

ICP PARAMETER SHEET

Instrument Perkin Elmer ICP 5500
(Manufacturer/Model)

Nebulizer Cross-Flow Nebulizer

Wavelength 220

Grating UV grating - 2880 lines/mm; Visible grating - 1440 lines/mm

Resolution 0.027 nm

Focal Length 408 mm

Background Correction NONE

Interference Correction NONE

Forward Power 1.25 Kilowatts

Reflected Power < 10.0 watts

Plasma Frequency Crystal Controlled Power Supply (27.12 MHz)
(Stability 0.05 %)

Auxilliary Gas Flow Rate 0.2 Lpm

Sample Introduction Rate 1.75 ml/min

Calibration Standards and Calibration Check Samples 10.00 ppm and 5.00 ppm - Calibration Standards; 7.5 ppm - independent check sample.

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 44

Digestion Method NIOSH 7082 Laboratory _____

Experience with this Method 10 years _____

Analysis Method ICP Approval Signature:

Experience with this Method 12 years _____

	Gross Concentration of Lead (ppm)		
Sample ID No.	Aliquot 1	Aliquot 2	Aliquot 3
P-1	1070	1400	1340
P-2	54500	46900	57800
P-3	35200	32900	34300
P-4	1508	1180	1250
P-5	34600	33400	34100
D-1	5040	5010	4350
D-2	< 50.0	< 50.0	< 50.0
D-3	1050	1000	1030
D-4	< 50.0	65.7	50.3
D-5	5560	4540	4360

Reagent Blank

< 5.0 µg/sample (0.05 µg/ml

< 5.0 µg/sample

ICP PARAMETER SHEET

Instrument JARRELL-ASH ATOMCOMP 1160
(Manufacturer/Model)

Nebulizer FIXED CROSS FLOW

Wavelength 220.35 nm

Grating JARRELL-ASH 1411 DLAI

Resolution

Focal Length 1 m

Background Correction

Interference Correction

Forward Power 1.15 KW

Reflected Power < 5 W

Plasma Frequency 27.12

Auxilliary Gas Flow Rate NONE

Sample Introduction Rate 1.67 ml/min

Calibration Standards and Calibration Check Samples

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 45

Digestion Method NIOSH 7082 Laboratory _____

Experience with this Method _____ years _____

Analysis Method ICP Approval Signature:

Experience with this Method 6 years _____

Sample ID No.	Gross Concentration of Lead (ppm) Aliquot 1	Aliquot 2
P-1	1,720 ppm	1,810 ppm
P-2	115,000 ppm	94,700 ppm
P-3	36,900	37,400 ppm
P-4	1,940 ppm	1,990 ppm
P-5	37,200	36,400 ppm
D-1	4,170 ppm	4,750 ppm
D-2	270 ppm	150 ppm
D-3	1,200 ppm	1,140 ppm
D-4	160 ppm	< 50 ppm
D-5	4,540 ppm	4,590 ppm
Reagent Blank	10.1 ug/sample	

ICP PARAMETER SHEET

Instrument Jarrell-Ash 9000 Air Spectrometer
(Manufacturer/Model)

Nebulizer Fixed Cross Flow

Wavelength 2203.00

Grating 1516 groves/mm ruled grating at 500 nm

Resolution .045 nm, First Order, .023 nm, Second Order, .015 nm Thir

Focal Length Focal curve is 580 mm in length

Background Correction No

Interference Correction Yes Fe, Mg, Al

Forward Power 1.2 Kilometer

Reflected Power 0

Plasma Frequency

Auxilliary Gas Flow Rate 22 LPM

Sample Introduction Rate 2.7 ml per min

Calibration Standards and Calibration Check Samples

Fisher Lead Reference Solution 1,000 ppm ± 1%

NIST Reference Std QC 3469	Lead Reported 58.2 ug/f Actual 56.9 ug/f
NIST Reference Std QC 34370	Lead Reported 40 ug/f Actual 37.8 ug/f

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 46

Digestion Method NIOSH 7082 Laboratory _____

Experience with this Method 1MON. ~~years~~ _____

Analysis Method ICP Approval Signature: _____

Experience with this Method 7 years _____

Sample ID No.	Gross Concentration of Lead (ppm) Aliquot 1	Aliquot 2
P-1	1160	1280
P-2	84,000	Not available
P-3	32,000	30,800
P-4	1280	1330
P-5	28,600	30,200
D-1	3160	4110
D-2	160	80
D-3	840	840
D-4	70	70
D-5	3580	2670
Reagent Blank	0	
	0	

ICP PARAMETER SHEET

Instrument: Perkin Elmer 6000 ICP
(Manufacturer/Model)

Nebulizer: Cross Flow

Wavelength: 220. 353 nm

Grating: UV grating – holographic

Resolution: 0.001 nm

Focal Length: 408 mm

Background Correction: Yes

Interference Correction: Yes

Forward Power: 1.20 Kilowatts

Reflected Power: Less than 5 watts

Plasma Frequency: 27.12 MHz ISM Band

Auxilliary Gas Flow Rate: 0.6 L/min

Sample Introduction Rate: 1.1 mL/min

Calibration Standards and Calibration Check Samples

1. Calibration standards – 0.00 and 10.00 µg/mL
2. Check samples – 0.00 and 10.00 µg/mL
3. The 0.00 µg/mL check sample could not drift beyond ±0.05 ug/mL and the 10.00 µg/mL sample beyond 5% (9.50 and 10.50 µg/mL).
4. A manually plotted line using 0.00, 0.50, 3.00, and 10.00 µg/mL standards resulted in an r square value of 1.000.

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 47

Digestion Method NIOSH 7082 Laboratory _____

Experience with this Method 5 years _____

Analysis Method ICP Approval Signature:

Experience with this Method 7 years _____

Sample ID No.	Gross Concentration of Lead (ppm) Aliquot 1	Aliquot 2
P-1	1,600	1,500
P-2	110,000	110,000
P-3	36,000	36,000
P-4	1,700	1,900
P-5	36,000	37,000
D-1	4,400	4,500
D-2	110	100
D-3	1,200	1,200
D-4	82	130
D-5	4,500	5,300
Reagent Blank	<40	
	<40	

ICP PARAMETER SHEET

Instrument Thermo Jarrell Ash ICAP 9000
(Manufacturer/Model)

Nebulizer Fixed Cross Flow Pneumatic

Wavelength 2203.53 Å

Grating 1510 g/mm ruled @ 500 nm

Resolution 0.045 nm (1st order)

Focal Length 0.75 m

Background Correction Spectrum shifted, background point at 220.252 nm

Interference Correction Interferents: Ti, Cr, Al, Cu, Mn

Forward Power 1.1 kw

Reflected Power <10 w

Plasma Frequency 27.12 MH_z

Auxilliary Gas Flow Rate ~ 2 LPM

Sample Introduction Rate 1.75 ml/min

Calibration Standards and Calibration Check Samples

Standardization @ 10 mg/L, Check Standard @ 2 mg/L & 100 mg/L

Interference Check Standard @ 1 mg/L with interferents @ 200 mg/L

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 48

Digestion Method NIOSH 7082 Laboratory _____

Experience with this Method _____ years _____

Analysis Method ICP Approval Signature:

Experience with this Method 2 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1628	1693
P-2	83220	92530
P-3	36428	36410
P-4	1555	1451
P-5	35800	36910
D-1	5010	4057
D-2	< 200	< 200
D-3	1168	1224
D-4	< 200	< 200
D-5	4047	~~4253~~ 4352

Reagent Blank 0.1 µg/mL Pb

< 200 µg/g Pb

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No.: 49

Digestion Method NIOSH 7082 Laboratory _____

Experience with this Method 0 years _____

Analysis Method ICP Approval Signature:

Experience with this Method 8 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	2000	1400
P-2	70000	88000
P-3	35000	35000
P-4	1600	1700
P-5	37000	35000
D-1	3800	4400
D-2	61	< 35
D-3	1100	1000
D-4	< 40	< 34
D-5	3700	4700
Reagent Blank	Below detection limits for this wavelength which is 0.05 mg/L	

ICP PARAMETER SHEET

Instrument ARL 3510
(Manufacturer/Model)

Nebulizer Meinhard

Wavelength 220.353 nm

Grating 2400 groves/mm, Holographic

Resolution 0.0112 nm (Information from Factory Test)

Focal Length 1 meter

Background Correction Two point background correction may - but results checked at two other lead wavelengths, 283.3 and 405.7 nm.

Interference Correction

Forward Power 1200

Reflected Power 1

Plasma Frequency 27.12 MHz.

Auxilliary Gas Flow Rate 30 psi for coolant gas
18 psi for plasma gas

Sample Introduction Rate ~1 mL/min

Calibration Standards and Calibration Check Samples standards at 0, 10, 20, and 100 mg/L lead

Appendix E-5

Laboratory XRF Laboratories

EPA/RTI Round Robin for Lead In Paint and Dust

Round Robin No. 002 Lab ID No. 50

Digestion Method N/A Laboratory _____

Experience with this Method 9mo ~~years~~ _____

Analysis Method Lab XRF Approval Signature:

Experience with this Method 9mo ~~years~~ _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1300	1300
P-2	>50000	>50000
P-3	32510	29650
P-4	1300	1300
P-5	29450	31980
D-1	2951	2751
D-2	< 75	< 75
D-3	981	1007
D-4	< 75	< 75
D-5	2948	2921
Reagent Blank	N/A	
	N/A	
	N/A	
	N/A	

LABORATORY XRF PARAMETERS - PAINT

Sample Quantity 1 GRAM

Sample Preparation
Rotate bottle to compensate for absorption of sample. Weigh out 1 gram of sample. Place 1 gram aliquot into an XRF sample cup and seal with mylar film.

Instrument Outokumpu X-MET 820 Electronics

Description of X-ray Source Cd 109

Description of Secondary Target N/A

Description of Detector Proportional Counter

Reference Outokumpu Electronics

LABORATORY XRF PARAMETERS - PAINT

Counting Time 120 Seconds

Counting Rate N/A

Total Counts N/A

Calibration Standards Lead in Paint (Stds: 1100ppm, 4800ppm, 9800ppm, 28000ppm)

Results of Calibration Check Samples Sample #2396 (1500ppm) Sample #3017 (4000ppm)

LABORATORY XRF PARAMETERS - DUST

Sample Quantity 2 GRAMS

Sample Preparation
Rotate bottle to compensate for separation of sample. Weigh out 2 grams of sample. Place 2 gram aliquot into an XRF sample cup and seal with mylar film

Instrument Outokumpu Electronics X-MET 820

Description of X-ray Source Cd 109

Description of Secondary Target N/A

Description of Detector Proportional Counter

Reference Outokumpu Electronics

LABORATORY XRF PARAMETERS - DUST

Counting Time 120 Seconds

Counting Rate N/A

Total Counts N/A

Calibration Standards -- CIN 1 and BAL 1

Results of Calibration Check Samples

BAL-1 51ppm 54ppm

CIN-1 3734ppm 3739ppm

NIST 1648 (SRM DUST 6550ppm) 7248ppm

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 51

Digestion Method N/A Laboratory _____

Experience with this Method _____ years _____

Analysis Method Lab XRF Approval Signature:

Experience with this Method 2 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1200	1183
P-2	118327	118327
P-3	23112	23992
P-4	1112	1270
P-5	23816	23992
D-1	2775	2415
D-2	72	82
D-3	1074	1014
D-4	76	72
D-5	2435	2775
Reagent Blank	N/A	
	N/A	
	N/A	
	N/A	

LABORATORY XRF PARAMETERS - PAINT

Sample Quantity 1 gram

Sample Preparation
Sample was shaken then 1 gram was transferred to a 31 mm sample cup and covered with .2 mil polypropylene film.

Instrument XRF Kevex 0700 with Kevex 7000 micro ~~pulse~~ processor

Description of X-ray Source Rhodium, Atomic number 45

Description of Secondary Target Silver secondary target

Description of Detector Kevex Lithium drifter silicon detector head with beryllium window

Reference Kevex Standard 316 Stainless Steel

LABORATORY XRF PARAMETERS - PAINT

Counting Time 100 seconds

Counting Rate approx. 4000 cts/sec.

Total Counts approx. 400 000

Calibration Standards NBS 1579 cut to .05% with graphite powder. STDS concentration, 11.87%, 5.9% 0.19%, 0.09%, 0.05% (.9997 calibration coff.)

Results of Calibration Check Samples

Sample run on ICP lead 126% on XRF

LABORATORY XRF PARAMETERS - DUST

Sample Quantity 1 gram

Sample Preparation
Samples were shaken, then 1 gram of sample was transferred to a 31 mm sample cup and covered with .2 mil polypropylene film

Instrument Kevex XRF 0700 with Kevex 7000 microprocessor

Description of X-ray Source Rhodium Atomic #45

Description of Secondary Target Silver

Description of Detector Kevex Lithium drifted silicon detector head with berilium window.

Reference Kevex Standard 316 Stainless Steel.

LABORATORY XRF PARAMETERS - DUST

Counting Time 100 sec.

Counting Rate approx 4000 c.ts/sec.

Total Counts approx 400 000

Calibration Standards -- CIN 1 and BAL 1

Results of Calibration Check Samples No check samples available for dust. Although a paint sample was run against this calibration with 93.4 %R (against ICP method).

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 52

Digestion Method N/A Laboratory _____

Experience with this Method _____ years _____

Analysis Method Lab XRF Approval Signature:

Experience with this Method 4 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	934	879
P-2	129,600	133,300
P-3	25,440	24,780
P-4	881	906
P-5	24,340	24,420
D-1	2167	2133
D-2	71	73
D-3	1100	1100
D-4	78	75
D-5	2166	2200
Reagent Blank	N/A	
	N/A	
	N/A	
	N/A	

LABORATORY XRF PARAMETERS - PAINT

Sample Quantity

Sample Preparation

Instrument Kevex 770 Analyst

Description of X-ray Source Rhodium standard w/5mil. Be Window thickness; Voltage 0-60kV; Current 0-3.3mA

Description of Secondary Target Molybdenum

Description of Detector Cryostat; Energy Resolution 165eV FWHM measured for 5.9 KeV X-rays; Dewar capacity 30 liter.

Reference

LABORATORY XRF PARAMETERS - PAINT

Counting Time 100 sec

Counting Rate

Total Counts

Calibration Standards

2.0 wt% ; 5.70 wt% ; 10.40 wt%

11.90 wt% (NBS-1579) ; 18.80 wt%

Results of Calibration Check Samples

LABORATORY XRF PARAMETERS - DUST

Sample Quantity

Sample Preparation

Instrument Kevex 770 Analyst

Description of X-ray Source Rhodium Standard with 5 mil Be Window thickness; Voltage 0 - 60 KV; current 0 - 3.3 mA

Description of Secondary Target Molybdenum

Description of Detector Cryostat; Energy resolution 165 eV FWHM measured for 5.9 KeV x-rays; Dewar capacity 30 liters

Reference

LABORATORY XRF PARAMETERS - DUST

Counting Time 100 Sec.

Counting Rate _____

Total Counts _____

Calibration Standards -- CIN 1 and BAL 1

Results of Calibration Check Samples _____

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 53

Digestion Method N/A Laboratory _____

Experience with this Method _____ years _____

Analysis Method Lab XRF Approval Signature.

Experience with this Method 2 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	5434	5148
P-2	104,510	101,852
P-3	29,573	27,368
P-4	6,003	5,823
P-5	26,403	26,178
D-1	2,000	2,000
D-2	126	137
D-3	863	916
D-4	113	126
D-5	1,400	1,900
Reagent Blank	N/A	
	N/A	
	N/A	
	N/A	

LABORATORY XRF PARAMETERS - PAINT

Sample Quantity 0.20g (± 0.01g)

Sample Preparation

Sample bottle was rotated to insure mixture of sample material. The 0.20 gram of sample was weighed as combined with 1 gram of cellulose and 1 gram of zinc oxide in a plastic mixing vial with mixing balls (exact weights were recorded). The samples were then mixed for 10 minutes in a shaker mill. After mixing the samples were pressed into pellets using a Carver press. Each pellet was pressed to 10,000 lbs. for a minimum of 5 minutes. (NISTIR 89-4209)

Instrument Computerized Energy Dispersive X-ray Fluorescence System, Kevex 770/Delta

Description of X-ray Source Rhodium

Description of Secondary Target Zirconium

Description of Detector Lithium-drifted Silicon

Reference

LABORATORY XRF PARAMETERS - PAINT

Counting Time 300 seconds

Counting Rate See attached Table 1

Total Counts See attached Table 1

Calibration Standards NIST SRM1589 11.87 Pb in paint

Results of Calibration Check Samples

LABORATORY XRF PARAMETERS - DUST

Sample Quantity 100g

Sample Preparation

Sample bottles were rotated to insure proper mixing of sample material. A portion of undiluted sample was placed in a XRF sample cup with mylar film covering the bottom and microporous film over the top.

Instrument Computerized Energy Dispersive X-ray Fluorescence System, Kevex 770/Delta

Description of X-ray Source Rhodium

Description of Secondary Target Zirconium

Description of Detector Lithium-drifted Silicon

Reference

LABORATORY XRF PARAMETERS - DUST

Counting Time 200 seconds

Counting Rate See attached Table 1

Total Counts See attached Table 1

Calibration Standards -- CIN 1 and BAL 1

Results of Calibration Check Samples

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002

Lab ID No. 54

Digestion Method N/A

Experience with this Method _____ years

Laboratory _____

Analysis Method Lab XRF

Experience with this Method 3 years

Approval Signature: (Sandy M. Rodda)

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	819	782
P-2	61123	60677
P-3	21591	21766
P-4	800	761
P-5	21845	21556
D-1	2417	2444
D-2	98	114
D-3	1052	1067
D-4	118	111
D-5	2415	2424
Reagent Blank	N/A	
	N/A	
	N/A	
	N/A	

LABORATORY XRF PARAMETERS - PAINT

Sample Quantity 2 grams

Sample Preparation

Loose powder placed in sample cups sealed with polypropylene film.

Instrument KEVEX 770

Description of X-ray Source X-ray tube Kevex high output rhodium anode.

Description of Secondary Target Mo

Description of Detector SiLi

Reference

LABORATORY XRF PARAMETERS - PAINT

Counting Time 200

Counting Rate Counts/second

Total Counts DEAD TIME ~45%

Calibration Standards 10 STANDARDS were used

range from 11 - 21867 PPM

Results of Calibration Check Samples NO PAINT REFERENCE SAMPLES were used. Ref sample supplied were used. Calibrated using soil samples. REF CIN = 2801

REF BAL = 65

LABORATORY XRF PARAMETERS - DUST

Sample Quantity 2 grams

Sample Preparation

Loose powder placed in a sample cup sealed with polypropylene film.

Instrument KEVEX 770

Description of X-ray Source X-ray tube; KEVEX high output rhodium anode.

Description of Secondary Target Mo

Description of Detector Si Li

Reference

LABORATORY XRF PARAMETERS - DUST

Counting Time 200

Counting Rate COUNTS/SECOND

Total Counts DEAD TIME = ~45%

Calibration Standards -- CIN 1 and BAL 1

Results of Calibration Check Samples REF CIN = 2815

REF BAL = 67

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No.: 55

Digestion Method N/A Laboratory _____

Experience with this Method _____ years _____

Analysis Method Lab XRF Approval Signature:

Experience with this Method 3.5 year _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1006	910
P-2	10.5 %	10.4 %
P-3	31905	31228
P-4	973	1021
P-5	33982	32388
D-1	2489	2458
D-2	107	81
D-3	976	962
D-4	81	87
D-5	2441	2514
Reagent Blank	N/A	
	N/A	
	N/A	
	N/A	

LABORATORY XRF PARAMETERS - PAINT

Sample Quantity 2 - 2.5 grams

Sample Preparation

(See Attached)

Instrument Kevex Delta-770 Analyst (EDXRF)

Description of X-ray Source Rh x-ray tube; Maximum voltage: 60 KeV

Maximum amperage: 3.3 mA

Description of Secondary Target Silver secondary target with 0.051 mm

silver secondary target filter. KeV = 35, mA = 1.5

Description of Detector Silicon lithium drifted detector

Reference N/A

LABORATORY XRF PARAMETERS - PAINT

Counting Time Livetime: 200 seconds (35% deadtime)

Counting Rate Time constant: 1.5 microseconds

Total Counts N/A

Calibration Standards Matrix: soil and dust; Units (mg/kg Pb)

Soils: 17993, 3772, 2455, 1069, 995, 849, 443

Dust: 58

Results of Calibration Check Samples

ID	TRUE mg/kg Pb	AVERAGE mg/kg Pb	% RSD	RPD	N
QC1	(17993)	18106	0.5	0.6	6
QC2	(443)	458	4.0	3.3	3
QC3	(6550)	6737	2.6	1.3	3

QC1: High calibration soil standard
QC2: Low range calibration soil standard
QC3: NBS 1648 (Urban Particulate)
N: Number of measurements

LABORATORY XRF PARAMETERS - DUST

Sample Quantity 2 - 2.5 grams

Sample Preparation

(See Attached)

Instrument Kevex Delta-770 Analyst (EDXRF)

Description of X-ray Source Rh x-ray tube; Maximum voltage; 60 KeV

Maximum amperage: 3.3 mA

Description of Secondary Target Silver secondary target with 0.051 mm

silver secondary target filter. KeV = 35, mA = 1.5

Description of Detector Silicon lithium drifted detector

Reference N/A

LABORATORY XRF PARAMETERS - DUST

Counting Time Livetime: 200 seconds (35% deadtime)

Counting Rate Time constant: 1.5 microseconds

Total Counts N/A

Calibration Standards -- CIN 1 and BAL 1

Results of Calibration Check Samples

ID	TRUE mg/kg Pb	AVERAGE mg/kg Pb	% RSD	RPD	N
QC1	17993	15131	0.4	17.3	6
QC2	443	396	4.5	11.2	3
QC3	6550	6192	2.5	5.6	3

QC1: Soil
QC2: Soil
QC3: NBS 1648 Urban Particulate
N: Number of measurements

EPA/RTI Round Robin for Lead in Paint and Dust

Round Robin No. 002 Lab ID No. 56

Digestion Method N/A Laboratory _____

Experience with this Method _____ years _____

Analysis Method Lab XRF Approval Signature:

Experience with this Method 5 years _____

	Gross Concentration of Lead (ppm)	
Sample ID No.	Aliquot 1	Aliquot 2
P-1	1010	1089
P-2	156559	159390
P-3	31370	30760
P-4	1059	1076
P-5	30780	31140
D-1	2703	2883
D-2	83	79
D-3	1134	1161
D-4	92	82
D-5	2716	2666
Reagent Blank	N/A	
	N/A	
	N/A	
	N/A	

LABORATORY XRF PARAMETERS - PAINT

Sample Quantity 2.0 grams per aliquot.

Sample Preparation
Sample vial was rotated for approx. 2 minutes to blend. Two aliquots were removed from each vial & transfered to Spex 31 mm Mylar cups. Samples analyzed using Mo x-rays through Mo prefilter, 35 KeV, 50μA. Pb Lβ line used for quantitation.

Instrument ORTEC TEFA II

Description of X-ray Source Mo/W dual anode, side window, oil cooled tube. 50 kV - 200μA maximum power.

Description of Secondary Target Mo prefilter

Description of Detector Si Li, Liquid Nitrogen cooled 1500 V potential; 165 eV resolution at 5.9 keV

Reference

LABORATORY XRF PARAMETERS - PAINT

Counting Time 200 seconds livetime

Counting Rate

Total Counts

Calibration Standards CIN 1 & BAL 1 (duplicate analysis)

NIST SRM 2704 (River Sediment @ 161 µg/g Pb)

Results of Calibration Check Samples CIN 1 = 62 µg/g Pb

BAL 1 = 2293 µg/g Pb ; CANMET Non-ferrous

dust, PD-1 = 28910 µg/g Pb (certified at 27500 µg/g)

LABORATORY XRF PARAMETERS - DUST

Sample Quantity See Paint.

Sample Preparation See Paint.

Instrument See Paint.

Description of X-ray Source See Paint

Description of Secondary Target See paint

Description of Detector See Paint

Reference

LABORATORY XRF PARAMETERS - DUST

Counting Time 200 seconds livetime

Counting Rate

Total Counts

Calibration Standards -- CIN 1 and BAL 1

Results of Calibration Check Samples CIN 1: 66 µg/g Pb

BAL 1 = 2321 µg/g Pb ; NIST SRM 2704 = 138 µg/g Pb (Certified at 161 µg/g).

Appendix F

Letter sent to Laboratories Reporting Preliminary Results of Round-Robin

RESEARCH TRIANGLE INSTITUTE

/RTI

Center for Environmental Measurements and Quality Assurance

October 13, 1992

Mr. Terry Burke
Wisconsin Occupational Health Laboratory
Department of Hygiene
979 Jonathon Drive
Madison, WI 53713

Dear Mr. Burke:

A statistical analysis of the results of the recent RTI/EPA round robin for lead in paint and dust is being finalized, and consensus values for concentrations of the samples have been determined. These values are presented in the enclosed tables that will be included in, "Preparation and Evaluation of Lead-based Paint Contaminated Method Evaluation Materials," as presented at the Lead Symposium of the American Chemical Society meeting in August, 1992. The paper, to be a part of the proceedings of the symposium, is currently being reviewed by EPA and, upon clearance, will be sent to all laboratories that participated in the round robin. It will include the consensus values for the concentration of the method evaluation samples, a comparision of statistically significant differences in the analytical methods, and inter- and intra-laboratory precision for these methods.

All laboratories received 10 samples for analysis, 5 paint and 5 dust samples. The samples from each matrix included duplicate bottles of one high level and one low level method evaluation material prepared by RTI, and one SRM. For example, the paint samples were comprised of one high paint material (P-3 and P-5), one low paint material (P-1 and P-4), and a paint SRM (P-2, NIST SRM 1579). The dust samples included one high, post-abatement dust (D-1 and D-5), one low household dust material (D-2 and D-4), and one sediment SRM (D-3, NIST SRM 2711). In order to provide information that will enable your laboratory to compare the results of its analysis with the consensus values, enclosed are two tables from the draft paper that provide the consensus values for the paint and dust samples, as determined from a "grand mean" of the

Post Office Box 12194 Research Triangle Park, North Carolina 27709-2194
Telephone 919 541-6914 Fax: 919 541-5929

digestive methods (hotplate and microwave digestion, followed by AAS or ICP analysis). Results from analysis by laboratory X-ray fluorescence were not included in the "grand mean" consensus values because this method exhibited a negative bias across the matrices.

A description of the preparation of the samples, and methodology used for the verification of the method evaluation materials will be included in an RTI report which is currently being prepared. The report will include a complete statistical analysis of the data, as well as a summary of any problems encountered by the laboratories in the analysis of the samples. We expect that the report will be distributed to the participating laboratories by the end of the year.

Also enclosed is a brochure describing the Environmental Lead Proficiency Analytical Testing (ELPAT) Program sponsored by the American Industrial Hygiene Association (AIHA). A number of the laboratories that participated in the round have been interested in this program, which offers either proficiency testing or proficiency testing and accreditation. The first round is scheduled for November 1992.

Once again, we appreciate your participation in the round robin, and we will be forwarding to you soon a copy of the proceedings paper. In the meantime, we will be happy to provide assistance if you have questions.

Sincerely,

Emily Williams

Emily Williams

Table 4. Mean and Consensus Values for Round Robin Paint Samples

Matrix	Sample No.	Method	Mean ± SD (%RSD), ppm	Consensus Mean[a] ± SD (%RSD), ppm
High paint	P-3, P-5	MW/AAS	41,281 ± 1,274 (3.1)	37,632 ± 449 (1.2)
		HP/AAS	36,921 ± 713 (1.9)	37,632 ± 449 (1.2)
		MW/ICP	36,654 ± 672 (1.8)	37,632 ± 449 (1.2)
		HP/ICP	35,670 ± 796 (2.2)	37,632 ± 449 (1.2)
		Lab XRF	27,404 ± 1,567 (5.7)	37,632 ± 449 (1.2)
Low paint	P-1, P-4	MW/AAS	1,896 ± 63 (3.3)	1,690 ± 32 (1.9)
		HP/AAS	1,661 ± 74 (4.5)	1,690 ± 32 (1.9)
		MW/ICP	1,603 ± 45 (2.8)	1,690 ± 32 (1.9)
		HP/ICP	1,600 ± 66 (4.1)	1,690 ± 32 (1.9)
		Lab XRF	1,034 ± 76 (7.4)	1,690 ± 32 (1.9)
Paint SRM	P-2	MW/AAS	122,432 ± 6,507 (5.3)	109,859 ± 3,289 (3.0)
		HP/AAS	104,340 ± 8,681 (8.3)	109,859 ± 3,289 (3.0)
		MW/ICP	118,281 ± 2,476 (2.1)	109,859 ± 3,289 (3.0)
		HP/ICP	94,382 ± 7,021 (7.4)	109,859 ± 3,289 (3.0)
		Lab XRF	112,721 ± 13,259 (11.8)	109,859 ± 3,289 (3.0)

[a]Lab XRF not included in consensus value determination.

Table 5. Mean and Consensus Values for Round Robin Dust Samples

Matrix	Sample No.	Method	Mean ± SD (% RSD), ppm	Consensus Mean[a] ± SD (% RSD), ppm
High dust	D-1, D-5	MW/AAS	4,847 ± 127 (2.6)	4,550 ± 60 (1.3)
		HP/AAS	4,677 ± 103 (2.2)	4,550 ± 60 (1.3)
		MW/ICP	4,281 ± 113 (2.6)	4,550 ± 60 (1.3)
		HP/ICP	4,397 ± 133 (3.0)	4,550 ± 60 (1.3)
		Lab XRF	2,485 ± 117 (4.7)	4,550 ± 60 (1.3)
Low dust	D-2, D-4	MW/AAS	114 ± 6 (5.3)	104 ± 3 (2.9)
		HP/AAS	108 ± 7 (6.5)	104 ± 3 (2.9)
		MW/ICP	98 ± 3 (3.1)	104 ± 3 (2.9)
		HP/ICP	98 ± 9 (9.2)	104 ± 3 (2.9)
		Lab XRF	93 ± 8 (8.6)	105 ± 3 (2.9)
Dust SRM	D-2	MW/AAS	1,327 ± 72 (5.4)	1,186 ± 23 (1.9)
		HP/AAS	1,173 ± 32 (2.7)	1,186 ± 23 (1.9)
		MW/ICP	1,133 ± 24 (2.1)	1,186 ± 23 (1.9)
		HP/ICP	1,112 ± 42 (3.8)	1,186 ± 23 (1.9)
		Lab XRF	1,029 ± 33 (3.2)	1,186 ± 23 (1.9)

[a]Lab XRF not included in consensus value determination.

Appendix G

Statistical Analysis of Results

Appendix G-1

Report of Statistical Analysis by Larry Myers

Statistical Analyses

Brief Summaries of the statistical methods and results are provided below. All statistical concepts, models and methods, including analysis of variance and interaction, are treated in Kleinbaum and Kupper (1978, Applied Regression Analysis and other Multivariable Methods, Duxbury Press, North Scituate, Massachusetts).

1. Censored, Missing and Outlying Values

42 labs were to analyze the panel of 10 samples in duplicate, which would yield 840 results. 848 results were received because two individual results were missing, and one lab did triplicate analyses on each sample. 28 results were reported as less than a specified level. These censored values, most of which occurred in the low dust samples, were removed prior to statistical analysis. This reduced the dataset to 820 results. An additional 28 observations were removed as outliers. All analyses reported below were based on the remaining 792 observations.

Determination of Outliers

The following approach was used to determine outliers among the 820 nonmissing, noncensored observations. For each of the six combinations of matrix (dust, paint) and level (high, low, SRM), a nominal concentration X was obtained as the median of all reported results from methods 1 through 4. (Method 5 was clearly producing lower values than the others.) The recovery was then calculated for each individual result as the ratio Y/X of the reported concentration divided by the nominal concentration. Using recoveries between 0.35 and 2, the average and standard deviation of recovery was calculated separately for each of the thirty method(5)-by-matrix(2)-by-level(3) combinations. The restriction to recoveries between .35 and 2 is a prescreen intended to remove grosser outliers which can distort the mean and standard deviation. These statistics were merged back onto the original raw data and a score was calculated for the recovery of each reported result, by subtracting the average recovery and

dividing by the standard deviation of recovery for the given condition. Any measurement whose absolute score exceeded 2.576 was excluded as an outlier. This corresponds to the upper and lower one-half of one percent of a normal distribution. This resulted in the exclusion of an additional 28 observations.

2. Consensus values (nominal concentrations)

Consensus values or nominal concentrations for each of the six samples were calculated as the simple average of the method-specific averages, using nonmissing, noncensored, nonoutlying values from the four wet chemical (extraction) methods. The XRF method was excluded from the calculation of nominal values because of a pronounced negative bias relative to the other methods.

3. Tests for sample homogeneity.

The non-SRM samples were supplied as blinded duplicates. For these samples it is possible to test for homogeneity of the parent stocks using two-way analysis of variance, treating sampling, analysis, and their interaction as random effects. {That is, laboratories within a method, and replicate samples selected form the same parent stock, such as D-2 and D-4, were both viewed as random selection from a (normally distributed) population of same. The assumption of random effects is appropriate in order to generalize results to a larger population of laboratories.} This model was fit separately to all 20 combinations of method(5)-by-matrix(2)-by-level(2) which involved non-SRM samples.

A preliminary test for the absence of interaction between sample and laboratory indicated that this assumption was reasonable. (Only one of twenty interaction tests was significant at the 5% level (low dust, method 1, $.025<p<.05$). This is the expected number of rejections by chance alone, under the null hypothesis of no interaction.) Accepting the hypothesis of no interaction means that the contributions of sampling and analysis to the total variation can be thought of simply as additive.

Only one of twenty tests for sample main effects was significant (low dust, method 4, $.025<p<.05$). The other cases were nowhere near significant; in fact, most of the F values were below one. It thus appears that the bulk sample materials prepared by RTI are homogenous.

The results of these tests for interaction and sample main effects are essentially the same regardless of whether the original reported value or its logarithm are used for the analysis. The estimate of the coefficient of variation due to sampling was zero in sixteen of the twenty cases (80%), and is 9% or less in every case. On the average, over the twenty cases, the sampling component of variance accounts for 1.37% of the total variance. A 95% upper confidence limit for the sampling coefficient of variance is below 2.5%. Roughly speaking, we can therefore be 95% sure that 95% of all subsamples selected by these procedures contain within 5% (between 95% and 105%) of the overall average concentration.

The low dust samples produced the only significant interaction and sample main effect, as well as most of the censored values. They are apparently pushing on the detection limit.

4. Repeatability and Reproducibility

Estimates of repeatability and reproducibility coefficients of variation (CV) for each method were determined. The repeatability CV is the within-lab CV, while the reproducibility CV incorporates both within-lab and between-lab variation. These precision measures have been obtained by pooling information over the samples, using the logarithm of ppm to approximately stabilize variance. The variances corresponding to these CV's, i.e. the squares of the CV's, were estimated using restricted maximum likelihood estimation, and a two-way analysis-of-variance model with sample a fixed effect, and laboratory and interaction as random effects, as in Youden and Steiner (1975, p. 80).

The repeatabilities of the digestive methods are similar, in the 10 to 13 percent range. Using F-tests, XRF has significantly better repeatability than all other methods ($p<.001$). HP/ICP has the apparent worst repeatability, and is significantly less

repeatable than each of the other methods ($p<.05$ for each comparison). None of the other repeatability comparisons approaches significance.

The reproducibility estimates of the two MW methods are similar and lower than those of the HP and XRF methods. Formal comparisons are difficult because of the complex probability distribution of the reproducibility estimate, exacerbated by the imbalance resulting from censoring and deletion of outliers. Using Satterwaite's approximation to the degrees of freedom, MW/ICP is significantly more reproducible at the 1% level than XRF and both of the HP methods.

Appendix G-2

Review of Statistical Analysis by Jack Suggs

Review of Statistical Analysis by Jack Suggs

The results shown in Table 7 were taken from Larry Myers' original report. The concentration averages, $\bar{X}$, are expressed in original units (ppm). The standard deviations: sample-to-sample, within-lab, and between-lab are expressed as a percentage of level (based on analysis of logarithms).

1. For non-SRM samples, the sample-to-sample variation was based on a two-way analysis of variance of logs with no interaction applied separately to all 20 combinations of methods (5)-by-matrix(2)-by-level(2). The standard deviation for samples (in percent) is equivalent to a percent-difference between samples. Only one case (low dust, method 4) was observed to have a significant percent difference between samples. In all other cases, the sample-to-sample differences were zero (16 out of 20 cases) or nowhere near significant. The conclusion is that bulk sample material prepared by RTI does not significantly contribute to the overall method variation in analysis.

2. The order (or ranking) of the methods with respect to averages is consistent and highly significant in this regard. Method 1 has the highest average on each of the six samples. The chance of this happening is 0.000064 if all the methods were equal. Also method 2 has the second highest average of 5 of the six samples. Method 5 also has the lowest average on 5 of 6 samples which is also significant.

The repeatability (within-lab) and reproducibility (between-lab) standard deviations are based on a one-way analysis of variance of log-recoveries ignoring sample-to-sample differences. (These differences are absorbed into the estimates of repeatability and reproducibility, which were shown above to be non-significant.) There were no sampling effects with regards to SRMs. These results came from Larry Myers original report.

1. Method 5 has the best repeatability in log units on all six samples. By the same logic applied to the ranking of the averages, this result is also highly significant. This may be due to the possibility that the log transformation did not sufficiently stabilize the variances and that method 5 is actually operating at a different apparent level than the other methods on some of the samples. At the same time method 5 was fairly consistent in repeatability across all levels. No other consistencies could be recognized.

2. The most important single measure of method performance is reproducibility because it reflects interlaboratory as well all within laboratory variability. Method 5 has the worst (highest) reproducibility for all three paint samples. Method 3 has the lowest (best) reproducibility on five of the six samples.

3. It is desirable to have a constant percent repeatability and reproducibility apply across all levels of measurement at least for a given method. Table 7 does not support this. However, regressions of repeatability and reproducibility versus level for each method may provide a useful way of estimating method variability given a specific level of measurement. Prediction intervals could be calculated at the 95% probability level to predict the occurrence of future values of repeatability and reproducibility for a given method and a given level of measurement.

   If the intercepts are forced through zero, the slope represents a percent change in repeatability or reproducibility for each unit change in measurement level.

4. Another estimation procedure along these lines would be to pool all information for each method separately (this includes paint, dust, SRMs) into an analysis of variance (one-way disregarding measurement level). As I stated

above, this represents an alternative to the regression approach which provides a "single" estimate of repeatability or reproducibility as a function (or percentage of level).

Appendix G-3

Raw Data File

LEGEND
(Appendix G-3)

OBS = Reported Result

BA = Laboratory Code

LEVEL = Concentration Level
- L = Low
- H = High
- S = SRM

SAM = Sample Number
- P = Paint
- D = Dust

REP = Replicate Number

CEN = Censored Data - Data reported as less than a specified level

CONC = Concentration (µg/g)

ANAL = Analytical Method
- ICP = Inductively Coupled Plasma Emission Spectrometry
- AA = Atomic Absorption Spectrometry

EXTR = Extraction Method
- NIO = NIOSH Method 7082
- EPA = EPA/AREAL Method

CONCAT = Concentration Category
- \+ = Reported
- m = Missing

OBS	BA	LEVEL	SAM	REP	CEN	CONC	ANAL	EXTR	CONCAT
1	42	L	P-1	1		1600	ICP	NIO	+
2	42	L	P-1	2		1500	ICP	NIO	+
3	42	L	P-4	1		1700	ICP	NIO	+
4	42	L	P-4	2		1900	ICP	NIO	+
5	42	H	P-3	1		36000	ICP	NIO	+
6	42	H	P-3	2		36000	ICP	NIO	+
7	42	H	P-5	1		36000	ICP	NIO	+
8	42	H	P-5	2		37000	ICP	NIO	+
9	42	S	P-2	1		110000	ICP	NIO	+
10	42	S	P-2	2		110000	ICP	NIO	+
11	42	L	D-2	1		110	ICP	NIO	+
12	42	L	D-2	2		100	ICP	NIO	+
13	42	L	D-4	1		82	ICP	NIO	+
14	42	L	D-4	2		130	ICP	NIO	+
15	42	H	D-1	1		4400	ICP	NIO	+
16	42	H	D-1	2		4500	ICP	NIO	+
17	42	H	D-5	1		4500	ICP	NIO	+
18	42	H	D-5	2		5300	ICP	NIO	+
19	42	S	D-3	1		1200	ICP	NIO	+
20	42	S	D-3	2		1200	ICP	NIO	+
21	38	L	P-1	1		1160	ICP	NIO	+
22	38	L	P-1	2		1280	ICP	NIO	+
23	38	L	P-4	1		1280	ICP	NIO	+
24	38	L	P-4	2		1330	ICP	NIO	+
25	38	H	P-3	1		32000	ICP	NIO	+
26	38	H	P-3	2		30800	ICP	NIO	+
27	38	H	P-5	1		28600	ICP	NIO	+
28	38	H	P-5	2		30200	ICP	NIO	+
29	38	S	P-2	1		84000	ICP	NIO	+
30	38	S	P-2	2			ICP	NIO	m
31	38	L	D-2	1		160	ICP	NIO	+
32	38	L	D-2	2		80	ICP	NIO	+
33	38	L	D-4	1		70	ICP	NIO	+
34	38	L	D-4	2		70	ICP	NIO	+
35	38	H	D-1	1		3160	ICP	NIO	+
36	38	H	D-1	2		4110	ICP	NIO	+
37	38	H	D-5	1		3580	ICP	NIO	+
38	38	H	D-5	2		2670	ICP	NIO	+
39	38	S	D-3	1		840	ICP	NIO	+
40	38	S	D-3	2		840	ICP	NIO	+
41	33	L	P-1	1		1070	ICP	NIO	+
42	33	L	P-1	2		1400	ICP	NIO	+
43	33	L	P-1	3		1340	ICP	NIO	+
44	33	L	P-4	1		1500	ICP	NIO	+
45	33	L	P-4	2		1180	ICP	NIO	+
46	33	L	P-4	3		1250	ICP	NIO	+
47	33	H	P-3	1		35200	ICP	NIO	+
48	33	H	P-3	2		32900	ICP	NIO	+
49	33	H	P-3	3		34300	ICP	NIO	+
50	33	H	P-5	1		34600	ICP	NIO	+
51	33	H	P-5	2		33400	ICP	NIO	+
52	33	H	P-5	3		34100	ICP	NIO	+
53	33	S	P-2	1		54500	ICP	NIO	+
54	33	S	P-2	2		46900	ICP	NIO	+
55	33	S	P-2	3		57800	ICP	NIO	+
56	33	L	D-2	1	<	50	ICP	NIO	+
57	33	L	D-2	2	<	50	ICP	NIO	+
58	33	L	D-2	3	<	50	ICP	NIO	+

OBS	BA	LEVEL	SAM	REP	CEN	CONC	ANAL	EXTR	CONCAT
59	33	L	D-4	1	<	50	ICP	NIO	+
60	33	L	D-4	2		66	ICP	NIO	+
61	33	L	D-4	3		50	ICP	NIO	+
62	33	H	D-1	1		5040	ICP	NIO	+
63	33	H	D-1	2		5010	ICP	NIO	+
64	33	H	D-1	3		4350	ICP	NIO	+
65	33	H	D-5	1		5560	ICP	NIO	+
66	33	H	D-5	2		4540	ICP	NIO	+
67	33	H	D-5	3		4360	ICP	NIO	+
68	33	S	D-3	1		1050	ICP	NIO	+
69	33	S	D-3	2		1000	ICP	NIO	+
70	33	S	D-3	3		1030	ICP	NIO	+
71	28	L	P-1	1		2000	ICP	NIO	+
72	28	L	P-1	2		1400	ICP	NIO	+
73	28	L	P-4	1		1600	ICP	NIO	+
74	28	L	P-4	2		1700	ICP	NIO	+
75	28	H	P-3	1		35000	ICP	NIO	+
76	28	H	P-3	2		35000	ICP	NIO	+
77	28	H	P-5	1		37000	ICP	NIO	+
78	28	H	P-5	2		35000	ICP	NIO	+
79	28	S	P-2	1		70000	ICP	NIO	+
80	28	S	P-2	2		88000	ICP	NIO	+
81	28	L	D-2	1		61	ICP	NIO	+
82	28	L	D-2	2	<	35	ICP	NIO	+
83	28	L	D-4	1	<	40	ICP	NIO	+
84	28	L	D-4	2	<	34	ICP	NIO	+
85	28	H	D-1	1		3800	ICP	NIO	+
86	28	H	D-1	2		4400	ICP	NIO	+
87	28	H	D-5	1		3700	ICP	NIO	+
88	28	H	D-5	2		4700	ICP	NIO	+
89	28	S	D-3	1		1100	ICP	NIO	+
90	28	S	D-3	2		1000	ICP	NIO	+
91	23	L	P-1	1		1790	ICP	NIO	+
92	23	L	P-1	2		1615	ICP	NIO	+
93	23	L	P-4	1		1450	ICP	NIO	+
94	23	L	P-4	2		1630	ICP	NIO	+
95	23	H	P-3	1		34500	ICP	NIO	+
96	23	H	P-3	2		34700	ICP	NIO	+
97	23	H	P-5	1		34500	ICP	NIO	+
98	23	H	P-5	2		34100	ICP	NIO	+
99	23	S	P-2	1		119000	ICP	NIO	+
100	23	S	P-2	2		115000	ICP	NIO	+
101	23	L	D-2	1		93	ICP	NIO	+
102	23	L	D-2	2		108	ICP	NIO	+
103	23	L	D-4	1		74	ICP	NIO	+
104	23	L	D-4	2		90	ICP	NIO	+
105	23	H	D-1	1		4060	ICP	NIO	+
106	23	H	D-1	2		4460	ICP	NIO	+
107	23	H	D-5	1		4220	ICP	NIO	+
108	23	H	D-5	2		4110	ICP	NIO	+
109	23	S	D-3	1		1120	ICP	NIO	+
110	23	S	D-3	2		1100	ICP	NIO	+
111	44	L	P-1	1		1556	ICP	NIO	+
112	44	L	P-1	2		1537	ICP	NIO	+
113	44	L	P-4	1		1882	ICP	NIO	+
114	44	L	P-4	2		1744	ICP	NIO	+
115	44	H	P-3	1		37140	ICP	NIO	+
116	44	H	P-3	2		35870	ICP	NIO	+

OBS	BA	LEVEL	SAM	REP	CEN	CONC	ANAL	EXTR	CONCAT
117	44	H	P-5	1		36510	ICP	NIO	+
118	44	H	P-5	2		36980	ICP	NIO	+
119	44	S	P-2	1		110500	ICP	NIO	+
120	44	S	P-2	2		113400	ICP	NIO	+
121	44	L	D-2	1		102	ICP	NIO	+
122	44	L	D-2	2		100	ICP	NIO	+
123	44	L	D-4	1		104	ICP	NIO	+
124	44	L	D-4	2		97	ICP	NIO	+
125	44	H	D-1	1		4013	ICP	NIO	+
126	44	H	D-1	2		4414	ICP	NIO	+
127	44	H	D-5	1		4535	ICP	NIO	+
128	44	H	D-5	2		4532	ICP	NIO	+
129	44	S	D-3	1		1249	ICP	NIO	+
130	44	S	D-3	2		1220	ICP	NIO	+
131	18	L	P-1	1		1757	ICP	NIO	+
132	18	L	P-1	2		1685	ICP	NIO	+
133	18	L	P-4	1		1872	ICP	NIO	+
134	18	L	P-4	2		1607	ICP	NIO	+
135	18	H	P-3	1		47300	ICP	NIO	+
136	18	H	P-3	2		36540	ICP	NIO	+
137	18	H	P-5	1		41260	ICP	NIO	+
138	18	H	P-5	2		44340	ICP	NIO	+
139	18	S	P-2	1		114760	ICP	NIO	+
140	18	S	P-2	2		111620	ICP	NIO	+
141	18	L	D-2	1		150	ICP	NIO	+
142	18	L	D-2	2		142	ICP	NIO	+
143	18	L	D-4	1	<	100	ICP	NIO	+
144	18	L	D-4	2	<	100	ICP	NIO	+
145	18	H	D-1	1		3365	ICP	NIO	+
146	18	H	D-1	2		5033	ICP	NIO	+
147	18	H	D-5	1		5538	ICP	NIO	+
148	18	H	D-5	2		5112	ICP	NIO	+
149	18	S	D-3	1		1317	ICP	NIO	+
150	18	S	D-3	2		1241	ICP	NIO	+
151	3	L	P-1	1		1720	ICP	NIO	+
152	3	L	P-1	2		1810	ICP	NIO	+
153	3	L	P-4	1		1940	ICP	NIO	+
154	3	L	P-4	2		1990	ICP	NIO	+
155	3	H	P-3	1		36900	ICP	NIO	+
156	3	H	P-3	2		37400	ICP	NIO	+
157	3	H	P-5	1		37200	ICP	NIO	+
158	3	H	P-5	2		36400	ICP	NIO	+
159	3	S	P-2	1		115000	ICP	NIO	+
160	3	S	P-2	2		94700	ICP	NIO	+
161	3	L	D-2	1		270	ICP	NIO	+
162	3	L	D-2	2		150	ICP	NIO	+
163	3	L	D-4	1		160	ICP	NIO	+
164	3	L	D-4	2	<	50	ICP	NIO	+
165	3	H	D-1	1		4170	ICP	NIO	+
166	3	H	D-1	2		4750	ICP	NIO	+
167	3	H	D-5	1		4540	ICP	NIO	+
168	3	H	D-5	2		4590	ICP	NIO	+
169	3	S	D-3	1		1200	ICP	NIO	+
170	3	S	D-3	2		1140	ICP	NIO	+
171	46	L	P-1	1		1628	ICP	NIO	+
172	46	L	P-1	2		1693	ICP	NIO	+
173	46	L	P-4	1		1555	ICP	NIO	+
174	46	L	P-4	2		1451	ICP	NIO	+

OBS	BA	LEVEL	SAM	REP	CEN	CONC	ANAL	EXTR	CONCAT
175	46	H	P-3	1		36420	ICP	NIO	+
176	46	H	P-3	2		36410	ICP	NIO	+
177	46	H	P-5	1		35800	ICP	NIO	+
178	46	H	P-5	2		36910	ICP	NIO	+
179	46	S	P-2	1		83220	ICP	NIO	+
180	46	S	P-2	2		92530	ICP	NIO	+
181	46	L	D-2	1	<	200	ICP	NIO	+
182	46	L	D-2	2	<	200	ICP	NIO	+
183	46	L	D-4	1	<	200	ICP	NIO	+
184	46	L	D-4	2	<	200	ICP	NIO	+
185	46	H	D-1	1		5010	ICP	NIO	+
186	46	H	D-1	2		4057	ICP	NIO	+
187	46	H	D-5	1		4047	ICP	NIO	+
188	46	H	D-5	2		4352	ICP	NIO	+
189	46	S	D-3	1		1168	ICP	NIO	+
190	46	S	D-3	2		1224	ICP	NIO	+
191	45	L	P-1	1		1650	ICP	NIO	+
192	45	L	P-1	2		2330	ICP	NIO	+
193	45	L	P-4	1		1840	ICP	NIO	+
194	45	L	P-4	2		2010	ICP	NIO	+
195	45	H	P-3	1		34500	ICP	NIO	+
196	45	H	P-3	2		42200	ICP	NIO	+
197	45	H	P-5	1		34100	ICP	NIO	+
198	45	H	P-5	2		38700	ICP	NIO	+
199	45	S	P-2	1		78700	ICP	NIO	+
200	45	S	P-2	2		118000	ICP	NIO	+
201	45	L	D-2	1		98	ICP	NIO	+
202	45	L	D-2	2		54	ICP	NIO	+
203	45	L	D-4	1		90	ICP	NIO	+
204	45	L	D-4	2		48	ICP	NIO	+
205	45	H	D-1	1		3860	ICP	NIO	+
206	45	H	D-1	2		5950	ICP	NIO	+
207	45	H	D-5	1		3860	ICP	NIO	+
208	45	H	D-5	2		7150	ICP	NIO	+
209	45	S	D-3	1		1010	ICP	NIO	+
210	45	S	D-3	2		1830	ICP	NIO	+
211	20	L	P-1	1		5434	XRF	N/A	+
212	20	L	P-1	2		5148	XRF	N/A	+
213	20	L	P-4	1		6003	XRF	N/A	+
214	20	L	P-4	2		5823	XRF	N/A	+
215	20	H	P-3	1		29573	XRF	N/A	+
216	20	H	P-3	2		27368	XRF	N/A	+
217	20	H	P-5	1		26403	XRF	N/A	+
218	20	H	P-5	2		26178	XRF	N/A	+
219	20	S	P-2	1		104510	XRF	N/A	+
220	20	S	P-2	2		101852	XRF	N/A	+
221	20	L	D-2	1		126	XRF	N/A	+
222	20	L	D-2	2		137	XRF	N/A	+
223	20	L	D-4	1		113	XRF	N/A	+
224	20	L	D-4	2		126	XRF	N/A	+
225	20	H	D-1	1		2000	XRF	N/A	+
226	20	H	D-1	2		2000	XRF	N/A	+
227	20	H	D-5	1		1400	XRF	N/A	+
228	20	H	D-5	2		1900	XRF	N/A	+
229	20	S	D-3	1		863	XRF	N/A	+
230	20	S	D-3	2		916	XRF	N/A	+
231	25	L	P-1	1		1300	XRF	N/A	+
232	25	L	P-1	2		1300	XRF	N/A	+

OBS	BA	LEVEL	SAM	REP	CEN	CONC	ANAL	EXTR	CONCAT
233	25	L	P-4	1		1300	XRF	N/A	+
234	25	L	P-4	2		1300	XRF	N/A	+
235	25	H	P-3	1		32510	XRF	N/A	+
236	25	H	P-3	2		29650	XRF	N/A	+
237	25	H	P-5	1		29450	XRF	N/A	+
238	25	H	P-5	2		31980	XRF	N/A	+
239	25	S	P-2	1	>	50000	XRF	N/A	+
240	25	S	P-2	2	>	50000	XRF	N/A	+
241	25	L	D-2	1	<	75	XRF	N/A	+
242	25	L	D-2	2	<	75	XRF	N/A	+
243	25	L	D-4	1	<	75	XRF	N/A	+
244	25	L	D-4	2	<	75	XRF	N/A	+
245	25	H	D-1	1		2951	XRF	N/A	+
246	25	H	D-1	2		2751	XRF	N/A	+
247	25	H	D-5	1		2948	XRF	N/A	+
248	25	H	D-5	2		2921	XRF	N/A	+
249	25	S	D-3	1		981	XRF	N/A	+
250	25	S	D-3	2		1007	XRF	N/A	+
251	30	L	P-1	1		934	XRF	N/A	+
252	30	L	P-1	2		879	XRF	N/A	+
253	30	L	P-4	1		881	XRF	N/A	+
254	30	L	P-4	2		906	XRF	N/A	+
255	30	H	P-3	1		25440	XRF	N/A	+
256	30	H	P-3	2		24780	XRF	N/A	+
257	30	H	P-5	1		24340	XRF	N/A	+
258	30	H	P-5	2		24420	XRF	N/A	+
259	30	S	P-2	1		129600	XRF	N/A	+
260	30	S	P-2	2		133300	XRF	N/A	+
261	30	L	D-2	1		71	XRF	N/A	+
262	30	L	D-2	2		73	XRF	N/A	+
263	30	L	D-4	1		78	XRF	N/A	+
264	30	L	D-4	2		75	XRF	N/A	+
265	30	H	D-1	1		2167	XRF	N/A	+
266	30	H	D-1	2		2133	XRF	N/A	+
267	30	H	D-5	1		2166	XRF	N/A	+
268	30	H	D-5	2		2200	XRF	N/A	+
269	30	S	D-3	1		1100	XRF	N/A	+
270	30	S	D-3	2		1100	XRF	N/A	+
271	10	L	P-1	1		1200	XRF	N/A	+
272	10	L	P-1	2		1183	XRF	N/A	+
273	10	L	P-4	1		1112	XRF	N/A	+
274	10	L	P-4	2		1210	XRF	N/A	+
275	10	H	P-3	1		23112	XRF	N/A	+
276	10	H	P-3	2		23992	XRF	N/A	+
277	10	H	P-5	1		23816	XRF	N/A	+
278	10	H	P-5	2		23992	XRF	N/A	+
279	10	S	P-2	1		118327	XRF	N/A	+
280	10	S	P-2	2		118327	XRF	N/A	+
281	10	L	D-2	1		72	XRF	N/A	+
282	10	L	D-2	2		82	XRF	N/A	+
283	10	L	D-4	1		76	XRF	N/A	+
284	10	L	D-4	2		72	XRF	N/A	+
285	10	H	D-1	1		2775	XRF	N/A	+
286	10	H	D-1	2		2415	XRF	N/A	+
287	10	H	D-5	1		2435	XRF	N/A	+
288	10	H	D-5	2		2775	XRF	N/A	+
289	10	S	D-3	1		1074	XRF	N/A	+
290	10	S	D-3	2		1014	XRF	N/A	+

OBS	BA	LEVEL	SAM	REP	CEN	CONC	ANAL	EXTR	CONCAT
291	5	L	P-1	1		1006	XRF	N/A	+
292	5	L	P-1	2		910	XRF	N/A	+
293	5	L	P-4	1		973	XRF	N/A	+
294	5	L	P-4	2		1021	XRF	N/A	+
295	5	H	P-3	1		31905	XRF	N/A	+
296	5	H	P-3	2		31228	XRF	N/A	+
297	5	H	P-5	1		33982	XRF	N/A	+
298	5	H	P-5	2		32388	XRF	N/A	+
299	5	S	P-2	1		105000	XRF	N/A	+
300	5	S	P-2	2		104000	XRF	N/A	+
301	5	L	D-2	1		107	XRF	N/A	+
302	5	L	D-2	2		81	XRF	N/A	+
303	5	L	D-4	1		81	XRF	N/A	+
304	5	L	D-4	2		87	XRF	N/A	+
305	5	H	D-1	1		2489	XRF	N/A	+
306	5	H	D-1	2		2458	XRF	N/A	+
307	5	H	D-5	1		2441	XRF	N/A	+
308	5	H	D-5	2		2514	XRF	N/A	+
309	5	S	D-3	1		976	XRF	N/A	+
310	5	S	D-3	2		962	XRF	N/A	+
311	49	L	P-1	1		1010	XRF	N/A	+
312	49	L	P-1	2		1089	XRF	N/A	+
313	49	L	P-4	1		1059	XRF	N/A	+
314	49	L	P-4	2		1076	XRF	N/A	+
315	49	H	P-3	1		31370	XRF	N/A	+
316	49	H	P-3	2		30760	XRF	N/A	+
317	49	H	P-5	1		30780	XRF	N/A	+
318	49	H	P-5	2		31140	XRF	N/A	+
319	49	S	P-2	1		156550	XRF	N/A	+
320	49	S	P-2	2		159390	XRF	N/A	+
321	49	L	D-2	1		83	XRF	N/A	+
322	49	L	D-2	2		79	XRF	N/A	+
323	49	L	D-4	1		92	XRF	N/A	+
324	49	L	D-4	2		82	XRF	N/A	+
325	49	H	D-1	1		2703	XRF	N/A	+
326	49	H	D-1	2		2883	XRF	N/A	+
327	49	H	D-5	1		2716	XRF	N/A	+
328	49	H	D-5	2		2666	XRF	N/A	+
329	49	S	D-3	1		1134	XRF	N/A	+
330	49	S	D-3	2		1161	XRF	N/A	+
331	15	L	P-1	1		819	XRF	N/A	+
332	15	L	P-1	2		782	XRF	N/A	+
333	15	L	P-4	1		800	XRF	N/A	+
334	15	L	P-4	2		761	XRF	N/A	+
335	15	H	P-3	1		21591	XRF	N/A	+
336	15	H	P-3	2		21766	XRF	N/A	+
337	15	H	P-5	1		21845	XRF	N/A	+
338	15	H	P-5	2		21556	XRF	N/A	+
339	15	S	P-2	1		61123	XRF	N/A	+
340	15	S	P-2	2		60677	XRF	N/A	+
341	15	L	D-2	1		93	XRF	N/A	+
342	15	L	D-2	2		114	XRF	N/A	+
343	15	L	D-4	1		118	XRF	N/A	+
344	15	L	D-4	2		111	XRF	N/A	+
345	15	H	D-1	1		2417	XRF	N/A	+
346	15	H	D-1	2		2444	XRF	N/A	+
347	15	H	D-5	1		2415	XRF	N/A	+
348	15	H	D-5	2		2424	XRF	N/A	+

OBS	BA	LEVEL	SAM	REP	CEN	CONC	ANAL	EXTR	CONCAT
349	15	S	D-3	1		1052	XRF	N/A	+
350	15	S	D-3	2		1067	XRF	N/A	+
351	40	L	P-1	1		1544	AA	NIO	+
352	40	L	P-1	2		1438	AA	NIO	+
353	40	L	P-4	1		1446	AA	NIO	+
354	40	L	P-4	2		1458	AA	NIO	+
355	40	H	P-3	1		36790	AA	NIO	+
356	40	H	P-3	2		42605	AA	NIO	+
357	40	H	P-5	1		37144	AA	NIO	+
358	40	H	P-5	2		35990	AA	NIO	+
359	40	S	P-2	1		116025	AA	NIO	+
360	40	S	P-2	2		99577	AA	NIO	+
361	40	L	D-2	1		96	AA	NIO	+
362	40	L	D-2	2		100	AA	NIO	+
363	40	L	D-4	1		110	AA	NIO	+
364	40	L	D-4	2		110	AA	NIO	+
365	40	H	D-1	1		4464	AA	NIO	+
366	40	H	D-1	2		4504	AA	NIO	+
367	40	H	D-5	1		4333	AA	NIO	+
368	40	H	D-5	2		4669	AA	NIO	+
369	40	S	D-3	1		1067	AA	NIO	+
370	40	S	D-3	2		1113	AA	NIO	+
371	36	L	P-1	1		1510	AA	NIO	+
372	36	L	P-1	2		1790	AA	NIO	+
373	36	L	P-4	1		1940	AA	NIO	+
374	36	L	P-4	2		1790	AA	NIO	+
375	36	H	P-3	1		33500	AA	NIO	+
376	36	H	P-3	2		39500	AA	NIO	+
377	36	H	P-5	1		36900	AA	NIO	+
378	36	H	P-5	2		41600	AA	NIO	+
379	36	S	P-2	1		102000	AA	NIO	+
380	36	S	P-2	2		111000	AA	NIO	+
381	36	L	D-2	1	<	100	AA	NIO	+
382	36	L	D-2	2		140	AA	NIO	+
383	36	L	D-4	1		108	AA	NIO	+
384	36	L	D-4	2		171	AA	NIO	+
385	36	H	D-1	1		3990	AA	NIO	+
386	36	H	D-1	2		4390	AA	NIO	+
387	36	H	D-5	1		4603	AA	NIO	+
388	36	H	D-5	2		5710	AA	NIO	+
389	36	S	D-3	1		1130	AA	NIO	+
390	36	S	D-3	2		1240	AA	NIO	+
391	31	L	P-1	1		1790	AA	NIO	+
392	31	L	P-1	2		1700	AA	NIO	+
393	31	L	P-4	1		2030	AA	NIO	+
394	31	L	P-4	2		1990	AA	NIO	+
395	31	H	P-3	1		41000	AA	NIO	+
396	31	H	P-3	2		39500	AA	NIO	+
397	31	H	P-5	1		43600	AA	NIO	+
398	31	H	P-5	2		46300	AA	NIO	+
399	31	S	P-2	1		140000	AA	NIO	+
400	31	S	P-2	2		132000	AA	NIO	+
401	31	L	D-2	1		116	AA	NIO	+
402	31	L	D-2	2		98	AA	NIO	+
403	31	L	D-4	1		130	AA	NIO	+
404	31	L	D-4	2		100	AA	NIO	+
405	31	H	D-1	1		5300	AA	NIO	+
406	31	H	D-1	2		5740	AA	NIO	+

OBS	BA	LEVEL	SAM	REP	CEN	CONC	ANAL	EXTR	CONCAT
407	31	H	D-5	1		4990	AA	NIO	+
408	31	H	D-5	2		5280	AA	NIO	+
409	31	S	D-3	1		1260	AA	NIO	+
410	31	S	D-3	2		1290	AA	NIO	+
411	26	L	P-1	1		2020	AA	NIO	+
412	26	L	P-1	2		1640	AA	NIO	+
413	26	L	P-4	1		1760	AA	NIO	+
414	26	L	P-4	2		1900	AA	NIO	+
415	26	H	P-3	1		39000	AA	NIO	+
416	26	H	P-3	2		38400	AA	NIO	+
417	26	H	P-5	1		38700	AA	NIO	+
418	26	H	P-5	2		38600	AA	NIO	+
419	26	S	P-2	1		112000	AA	NIO	+
420	26	S	P-2	2		113000	AA	NIO	+
421	26	L	D-2	1	<	300	AA	NIO	+
422	26	L	D-2	2	<	300	AA	NIO	+
423	26	L	D-4	1	<	300	AA	NIO	+
424	26	L	D-4	2	<	300	AA	NIO	+
425	26	H	D-1	1		4680	AA	NIO	+
426	26	H	D-1	2		4150	AA	NIO	+
427	26	H	D-5	1		5080	AA	NIO	+
428	26	H	D-5	2		4760	AA	NIO	+
429	26	S	D-3	1		1180	AA	NIO	+
430	26	S	D-3	2		1320	AA	NIO	+
431	21	L	P-1	1		1696	AA	NIO	+
432	21	L	P-1	2		1324	AA	NIO	+
433	21	L	P-4	1		1146	AA	NIO	+
434	21	L	P-4	2		1080	AA	NIO	+
435	21	H	P-3	1		34991	AA	NIO	+
436	21	H	P-3	2		33550	AA	NIO	+
437	21	H	P-5	1		35010	AA	NIO	+
438	21	H	P-5	2		34140	AA	NIO	+
439	21	S	P-2	1		118820	AA	NIO	+
440	21	S	P-2	2		115359	AA	NIO	+
441	21	L	D-2	1		97	AA	NIO	+
442	21	L	D-2	2		100	AA	NIO	+
443	21	L	D-4	1		92	AA	NIO	+
444	21	L	D-4	2		96	AA	NIO	+
445	21	H	D-1	1		4840	AA	NIO	+
446	21	H	D-1	2		4709	AA	NIO	+
447	21	H	D-5	1		4694	AA	NIO	+
448	21	H	D-5	2		4520	AA	NIO	+
449	21	S	D-3	1		960	AA	NIO	+
450	21	S	D-3	2		960	AA	NIO	+
451	16	L	P-1	1		1350	AA	NIO	+
452	16	L	P-1	2		1213	AA	NIO	+
453	16	L	P-4	1		1383	AA	NIO	+
454	16	L	P-4	2		1478	AA	NIO	+
455	16	H	P-3	1		33833	AA	NIO	+
456	16	H	P-3	2		36098	AA	NIO	+
457	16	H	P-5	1		32055	AA	NIO	+
458	16	H	P-5	2		35567	AA	NIO	+
459	16	S	P-2	1		105667	AA	NIO	+
460	16	S	P-2	2		110000	AA	NIO	+
461	16	L	D-2	1		89	AA	NIO	+
462	16	L	D-2	2		84	AA	NIO	+
463	16	L	D-4	1		65	AA	NIO	+
464	16	L	D-4	2		79	AA	NIO	+

OBS	BA	LEVEL	SAM	REP	CEN	CONC	ANAL	EXTR	CONCAT
465	16	H	D-1	1		3531	AA	NIO	+
466	16	H	D-1	2		4463	AA	NIO	+
467	16	H	D-5	1		3191	AA	NIO	+
468	16	H	D-5	2		4196	AA	NIO	+
469	16	S	D-3	1		1208	AA	NIO	+
470	16	S	D-3	2		1177	AA	NIO	+
471	11	L	P-1	1		1700	AA	NIO	+
472	11	L	P-1	2		1600	AA	NIO	+
473	11	L	P-4	1		1700	AA	NIO	+
474	11	L	P-4	2		1800	AA	NIO	+
475	11	H	P-3	1		36000	AA	NIO	+
476	11	H	P-3	2		35000	AA	NIO	+
477	11	H	P-5	1		36000	AA	NIO	+
478	11	H	P-5	2		37000	AA	NIO	+
479	11	S	P-2	1		46000	AA	NIO	+
480	11	S	P-2	2		55000	AA	NIO	+
481	11	L	D-2	1		140	AA	NIO	+
482	11	L	D-2	2		120	AA	NIO	+
483	11	L	D-4	1		110	AA	NIO	+
484	11	L	D-4	2		130	AA	NIO	+
485	11	H	D-1	1		4700	AA	NIO	+
486	11	H	D-1	2		4700	AA	NIO	+
487	11	H	D-5	1		4800	AA	NIO	+
488	11	H	D-5	2		4700	AA	NIO	+
489	11	S	D-3	1		1200	AA	NIO	+
490	11	S	D-3	2		1200	AA	NIO	+
491	6	L	P-1	1		1310	AA	NIO	+
492	6	L	P-1	2		2064	AA	NIO	+
493	6	L	P-4	1		1852	AA	NIO	+
494	6	L	P-4	2		2047	AA	NIO	+
495	6	H	P-3	1		36594	AA	NIO	+
496	6	H	P-3	2		35340	AA	NIO	+
497	6	H	P-5	1		34614	AA	NIO	+
498	6	H	P-5	2		35772	AA	NIO	+
499	6	S	P-2	1		14010	AA	NIO	+
500	6	S	P-2	2		5077	AA	NIO	+
501	6	L	D-2	1		214	AA	NIO	+
502	6	L	D-2	2		199	AA	NIO	+
503	6	L	D-4	1		85	AA	NIO	+
504	6	L	D-4	2		93	AA	NIO	+
505	6	H	D-1	1		4143	AA	NIO	+
506	6	H	D-1	2		3889	AA	NIO	+
507	6	H	D-5	1		5241	AA	NIO	+
508	6	H	D-5	2		5179	AA	NIO	+
509	6	S	D-3	1		1186	AA	NIO	+
510	6	S	D-3	2		1217	AA	NIO	+
511	1	L	P-1	1		1542	AA	NIO	+
512	1	L	P-1	2		2096	AA	NIO	+
513	1	L	P-4	1		1805	AA	NIO	+
514	1	L	P-4	2		1879	AA	NIO	+
515	1	H	P-3	1		37699	AA	NIO	+
516	1	H	P-3	2		35974	AA	NIO	+
517	1	H	P-5	1		37160	AA	NIO	+
518	1	H	P-5	2		37002	AA	NIO	+
519	1	S	P-2	1		93532	AA	NIO	+
520	1	S	P-2	2		99463	AA	NIO	+
521	1	L	D-2	1		109	AA	NIO	+
522	1	L	D-2	2		111	AA	NIO	+

OBS	BA	LEVEL	SAM	REP	CEN	CONC	ANAL	EXTR	CONCAT
523	1	L	D-4	1		109	AA	NIO	+
524	1	L	D-4	2		140	AA	NIO	+
525	1	H	D-1	1		4567	AA	NIO	+
526	1	H	D-1	2		5014	AA	NIO	+
527	1	H	D-5	1		5096	AA	NIO	+
528	1	H	D-5	2		4071	AA	NIO	+
529	1	S	D-3	1		1199	AA	NIO	+
530	1	S	D-3	2		1207	AA	NIO	+
531	39	L	P-1	1		1670	ICP	EPA	+
532	39	L	P-1	2		1220	ICP	EPA	+
533	39	L	P-4	1		1230	ICP	EPA	+
534	39	L	P-4	2		1490	ICP	EPA	+
535	39	H	P-3	1		37800	ICP	EPA	+
536	39	H	P-3	2		38000	ICP	EPA	+
537	39	H	P-5	1		35800	ICP	EPA	+
538	39	H	P-5	2		38700	ICP	EPA	+
539	39	S	P-2	1		135000	ICP	EPA	+
540	39	S	P-2	2		123000	ICP	EPA	+
541	39	L	D-2	1		87	ICP	EPA	+
542	39	L	D-2	2		108	ICP	EPA	+
543	39	L	D-4	1		97	ICP	EPA	+
544	39	L	D-4	2		84	ICP	EPA	+
545	39	H	D-1	1		3090	ICP	EPA	+
546	39	H	D-1	2		3690	ICP	EPA	+
547	39	H	D-5	1		3980	ICP	EPA	+
548	39	H	D-5	2		3840	ICP	EPA	+
549	39	S	D-3	1		1010	ICP	EPA	+
550	39	S	D-3	2		1060	ICP	EPA	+
551	34	L	P-1	1		1410	ICP	EPA	+
552	34	L	P-1	2		1750	ICP	EPA	+
553	34	L	P-4	1		1370	ICP	EPA	+
554	34	L	P-4	2		1600	ICP	EPA	+
555	34	H	P-3	1		34400	ICP	EPA	+
556	34	H	P-3	2		33800	ICP	EPA	+
557	34	H	P-5	1		35500	ICP	EPA	+
558	34	H	P-5	2		35400	ICP	EPA	+
559	34	S	P-2	1		116000	ICP	EPA	+
560	34	S	P-2	2		118000	ICP	EPA	+
561	34	L	D-2	1		107	ICP	EPA	+
562	34	L	D-2	2		98	ICP	EPA	+
563	34	L	D-4	1		88	ICP	EPA	+
564	34	L	D-4	2		103	ICP	EPA	+
565	34	H	D-1	1		3740	ICP	EPA	+
566	34	H	D-1	2		4230	ICP	EPA	+
567	34	H	D-5	1		3460	ICP	EPA	+
568	34	H	D-5	2		4680	ICP	EPA	+
569	34	S	D-3	1		1200	ICP	EPA	+
570	34	S	D-3	2		1150	ICP	EPA	+
571	29	L	P-1	1		1600	ICP	EPA	+
572	29	L	P-1	2		1400	ICP	EPA	+
573	29	L	P-4	1		2120	ICP	EPA	+
574	29	L	P-4	2		1590	ICP	EPA	+
575	29	H	P-3	1		35800	ICP	EPA	+
576	29	H	P-3	2		35000	ICP	EPA	+
577	29	H	P-5	1		39400	ICP	EPA	+
578	29	H	P-5	2		37600	ICP	EPA	+
579	29	S	P-2	1		116000	ICP	EPA	+
580	29	S	P-2	2		115000	ICP	EPA	+

OBS	BA	LEVEL	SAM	REP	CEN	CONC	ANAL	EXTR	CONCAT
581	29	L	D-2	1		126	ICP	EPA	+
582	29	L	D-2	2		98	ICP	EPA	+
583	29	L	D-4	1		88	ICP	EPA	+
584	29	L	D-4	2		98	ICP	EPA	+
585	29	H	D-1	1		4260	ICP	EPA	+
586	29	H	D-1	2		3940	ICP	EPA	+
587	29	H	D-5	1		4720	ICP	EPA	+
588	29	H	D-5	2		5360	ICP	EPA	+
589	29	S	D-3	1		1220	ICP	EPA	+
590	29	S	D-3	2		1150	ICP	EPA	+
591	9	L	P-1	1		1540	ICP	EPA	+
592	9	L	P-1	2		1680	ICP	EPA	+
593	9	L	P-4	1		1400	ICP	EPA	+
594	9	L	P-4	2		1410	ICP	EPA	+
595	9	H	P-3	1		38900	ICP	EPA	+
596	9	H	P-3	2		37600	ICP	EPA	+
597	9	H	P-5	1		36600	ICP	EPA	+
598	9	H	P-5	2		41000	ICP	EPA	+
599	9	S	P-2	1		119000	ICP	EPA	+
600	9	S	P-2	2		123000	ICP	EPA	+
601	9	L	D-2	1		74	ICP	EPA	+
602	9	L	D-2	2		83	ICP	EPA	+
603	9	L	D-4	1		72	ICP	EPA	+
604	9	L	D-4	2		84	ICP	EPA	+
605	9	H	D-1	1		5640	ICP	EPA	+
606	9	H	D-1	2		4840	ICP	EPA	+
607	9	H	D-5	1		4270	ICP	EPA	+
608	9	H	D-5	2		4190	ICP	EPA	+
609	9	S	D-3	1		950	ICP	EPA	+
610	9	S	D-3	2		1070	ICP	EPA	+
611	24	L	P-1	1			ICP	EPA	m
612	24	L	P-1	2		1700	ICP	EPA	+
613	24	L	P-4	1		1600	ICP	EPA	+
614	24	L	P-4	2		1800	ICP	EPA	+
615	24	H	P-3	1		39000	ICP	EPA	+
616	24	H	P-3	2		38000	ICP	EPA	+
617	24	H	P-5	1		39000	ICP	EPA	+
618	24	H	P-5	2		40000	ICP	EPA	+
619	24	S	P-2	1		120000	ICP	EPA	+
620	24	S	P-2	2		130000	ICP	EPA	+
621	24	L	D-2	1	<	22	ICP	EPA	+
622	24	L	D-2	2	<	22	ICP	EPA	+
623	24	L	D-4	1		100	ICP	EPA	+
624	24	L	D-4	2		31	ICP	EPA	+
625	24	H	D-1	1		4800	ICP	EPA	+
626	24	H	D-1	2		4300	ICP	EPA	+
627	24	H	D-5	1		4700	ICP	EPA	+
628	24	H	D-5	2		2500	ICP	EPA	+
629	24	S	D-3	1		1200	ICP	EPA	+
630	24	S	D-3	2		1200	ICP	EPA	+
631	19	L	P-1	1		1432	ICP	EPA	+
632	19	L	P-1	2		1408	ICP	EPA	+
633	19	L	P-4	1		1518	ICP	EPA	+
634	19	L	P-4	2		1502	ICP	EPA	+
635	19	H	P-3	1		34000	ICP	EPA	+
636	19	H	P-3	2		34100	ICP	EPA	+
637	19	H	P-5	1		32400	ICP	EPA	+
638	19	H	P-5	2		32600	ICP	EPA	+

OBS	BA	LEVEL	SAM	REP	CEN	CONC	ANAL	EXTR	CONCAT
639	19	S	P-2	1		109400	ICP	EPA	+
640	19	S	P-2	2		109600	ICP	EPA	+
641	19	L	D-2	1		87	ICP	EPA	+
642	19	L	D-2	2		89	ICP	EPA	+
643	19	L	D-4	1		145	ICP	EPA	+
644	19	L	D-4	2		98	ICP	EPA	+
645	19	H	D-1	1		4160	ICP	EPA	+
646	19	H	D-1	2		4170	ICP	EPA	+
647	19	H	D-5	1		3960	ICP	EPA	+
648	19	H	D-5	2		3960	ICP	EPA	+
649	19	S	D-3	1		1142	ICP	EPA	+
650	19	S	D-3	2		1104	ICP	EPA	+
651	14	L	P-1	1		1896	ICP	EPA	+
652	14	L	P-1	2		1529	ICP	EPA	+
653	14	L	P-4	1		1995	ICP	EPA	+
654	14	L	P-4	2		1775	ICP	EPA	+
655	14	H	P-3	1		42112	ICP	EPA	+
656	14	H	P-3	2		37519	ICP	EPA	+
657	14	H	P-5	1		37685	ICP	EPA	+
658	14	H	P-5	2		37270	ICP	EPA	+
659	14	S	P-2	1		126637	ICP	EPA	+
660	14	S	P-2	2		120216	ICP	EPA	+
661	14	L	D-2	1		211	ICP	EPA	+
662	14	L	D-2	2		101	ICP	EPA	+
663	14	L	D-4	1		99	ICP	EPA	+
664	14	L	D-4	2		98	ICP	EPA	+
665	14	H	D-1	1		4980	ICP	EPA	+
666	14	H	D-1	2		4443	ICP	EPA	+
667	14	H	D-5	1		4258	ICP	EPA	+
668	14	H	D-5	2		4026	ICP	EPA	+
669	14	S	D-3	1		1192	ICP	EPA	+
670	14	S	D-3	2		1206	ICP	EPA	+
671	4	L	P-1	1		1500	ICP	EPA	+
672	4	L	P-1	2		1880	ICP	EPA	+
673	4	L	P-4	1		1550	ICP	EPA	+
674	4	L	P-4	2		1830	ICP	EPA	+
675	4	H	P-3	1		35200	ICP	EPA	+
676	4	H	P-3	2		36700	ICP	EPA	+
677	4	H	P-5	1		33700	ICP	EPA	+
678	4	H	P-5	2		35200	ICP	EPA	+
679	4	S	P-2	1		117000	ICP	EPA	+
680	4	S	P-2	2		120000	ICP	EPA	+
681	4	L	D-2	1		80	ICP	EPA	+
682	4	L	D-2	2		140	ICP	EPA	+
683	4	L	D-4	1		170	ICP	EPA	+
684	4	L	D-4	2		110	ICP	EPA	+
685	4	H	D-1	1		4070	ICP	EPA	+
686	4	H	D-1	2		4960	ICP	EPA	+
687	4	H	D-5	1		4110	ICP	EPA	+
688	4	H	D-5	2		3900	ICP	EPA	+
689	4	S	D-3	1		1170	ICP	EPA	+
690	4	S	D-3	2		1180	ICP	EPA	+
691	43	L	P-1	1		1640	ICP	EPA	+
692	43	L	P-1	2	<	10	ICP	EPA	+
693	43	L	P-4	1		1490	ICP	EPA	+
694	43	L	P-4	2		1980	ICP	EPA	+
695	43	H	P-3	1		36100	ICP	EPA	+
696	43	H	P-3	2		35600	ICP	EPA	+

OBS	BA	LEVEL	SAM	REP	CEN	CONC	ANAL	EXTR	CONCAT
697	43	H	P-5	1		35400	ICP	EPA	+
698	43	H	P-5	2		25000	ICP	EPA	+
699	43	S	P-2	1		112000	ICP	EPA	+
700	43	S	P-2	2		99200	ICP	EPA	+
701	43	L	D-2	1		90	ICP	EPA	+
702	43	L	D-2	2		85	ICP	EPA	+
703	43	L	D-4	1		125	ICP	EPA	+
704	43	L	D-4	2		100	ICP	EPA	+
705	43	H	D-1	1		3980	ICP	EPA	+
706	43	H	D-1	2		4620	ICP	EPA	+
707	43	H	D-5	1		3500	ICP	EPA	+
708	43	H	D-5	2		5010	ICP	EPA	+
709	43	S	D-3	1		1010	ICP	EPA	+
710	43	S	D-3	2		1180	ICP	EPA	+
711	12	L	P-1	1		1810	ICP	EPA	+
712	12	L	P-1	2		1810	ICP	EPA	+
713	12	L	P-4	1		1880	ICP	EPA	+
714	12	L	P-4	2		2010	ICP	EPA	+
715	12	H	P-3	1		40500	ICP	EPA	+
716	12	H	P-3	2		41800	ICP	EPA	+
717	12	H	P-5	1		43300	ICP	EPA	+
718	12	H	P-5	2		46300	ICP	EPA	+
719	12	S	P-2	1		114000	ICP	EPA	+
720	12	S	P-2	2		116000	ICP	EPA	+
721	12	L	D-2	1		99	ICP	EPA	+
722	12	L	D-2	2		98	ICP	EPA	+
723	12	L	D-4	1		128	ICP	EPA	+
724	12	L	D-4	2		98	ICP	EPA	+
725	12	H	D-1	1		4870	ICP	EPA	+
726	12	H	D-1	2		5130	ICP	EPA	+
727	12	H	D-5	1		5190	ICP	EPA	+
728	12	H	D-5	2		5580	ICP	EPA	+
729	12	S	D-3	1		1440	ICP	EPA	+
730	12	S	D-3	2		1490	ICP	EPA	+
731	37	L	P-1	1		1510	AA	EPA	+
732	37	L	P-1	2		2010	AA	EPA	+
733	37	L	P-4	1		2053	AA	EPA	+
734	37	L	P-4	2		1640	AA	EPA	+
735	37	H	P-3	1		34600	AA	EPA	+
736	37	H	P-3	2		40800	AA	EPA	+
737	37	H	P-5	1		37600	AA	EPA	+
738	37	H	P-5	2		41900	AA	EPA	+
739	37	S	P-2	1		110200	AA	EPA	+
740	37	S	P-2	2		117300	AA	EPA	+
741	37	L	D-2	1		115	AA	EPA	+
742	37	L	D-2	2		117	AA	EPA	+
743	37	L	D-4	1		116	AA	EPA	+
744	37	L	D-4	2		103	AA	EPA	+
745	37	H	D-1	1		4920	AA	EPA	+
746	37	H	D-1	2		4340	AA	EPA	+
747	37	H	D-5	1		4630	AA	EPA	+
748	37	H	D-5	2		4500	AA	EPA	+
749	37	S	D-3	1		1060	AA	EPA	+
750	37	S	D-3	2		1140	AA	EPA	+
751	32	L	P-1	1		1500	AA	EPA	+
752	32	L	P-1	2		1900	AA	EPA	+
753	32	L	P-4	1		2300	AA	EPA	+
754	32	L	P-4	2		2000	AA	EPA	+

OBS	BA	LEVEL	SAM	REP	CEN	CONC	ANAL	EXTR	CONCAT
755	32	H	P-3	1		52000	AA	EPA	+
756	32	H	P-3	2		44000	AA	EPA	+
757	32	H	P-5	1		45000	AA	EPA	+
758	32	H	P-5	2		45000	AA	EPA	+
759	32	S	P-2	1		164000	AA	EPA	+
760	32	S	P-2	2		143000	AA	EPA	+
761	32	L	D-2	1		90	AA	EPA	+
762	32	L	D-2	2		91	AA	EPA	+
763	32	L	D-4	1		90	AA	EPA	+
764	32	L	D-4	2		100	AA	EPA	+
765	32	H	D-1	1		4800	AA	EPA	+
766	32	H	D-1	2		5300	AA	EPA	+
767	32	H	D-5	1		5100	AA	EPA	+
768	32	H	D-5	2		5400	AA	EPA	+
769	32	S	D-3	1		1100	AA	EPA	+
770	32	S	D-3	2		1200	AA	EPA	+
771	17	L	P-1	1		1920	AA	EPA	+
772	17	L	P-1	2		1720	AA	EPA	+
773	17	L	P-4	1		2050	AA	EPA	+
774	17	L	P-4	2		1740	AA	EPA	+
775	17	H	P-3	1		41500	AA	EPA	+
776	17	H	P-3	2		41300	AA	EPA	+
777	17	H	P-5	1		42700	AA	EPA	+
778	17	H	P-5	2		43600	AA	EPA	+
779	17	S	P-2	1		131000	AA	EPA	+
780	17	S	P-2	2		126000	AA	EPA	+
781	17	L	D-2	1		130	AA	EPA	+
782	17	L	D-2	2		130	AA	EPA	+
783	17	L	D-4	1		140	AA	EPA	+
784	17	L	D-4	2		140	AA	EPA	+
785	17	H	D-1	1		4720	AA	EPA	+
786	17	H	D-1	2		4930	AA	EPA	+
787	17	H	D-5	1		4800	AA	EPA	+
788	17	H	D-5	2		5040	AA	EPA	+
789	17	S	D-3	1		1340	AA	EPA	+
790	17	S	D-3	2		1340	AA	EPA	+
791	7	L	P-1	1		1801	AA	EPA	+
792	7	L	P-1	2		1735	AA	EPA	+
793	7	L	P-4	1		2165	AA	EPA	+
794	7	L	P-4	2		2280	AA	EPA	+
795	7	H	P-3	1		37700	AA	EPA	+
796	7	H	P-3	2		39430	AA	EPA	+
797	7	H	P-5	1		22440	AA	EPA	+
798	7	H	P-5	2		22640	AA	EPA	+
799	7	S	P-2	1		90520	AA	EPA	+
800	7	S	P-2	2		106200	AA	EPA	+
801	7	L	D-2	1		451	AA	EPA	+
802	7	L	D-2	2		465	AA	EPA	+
803	7	L	D-4	1		539	AA	EPA	+
804	7	L	D-4	2		567	AA	EPA	+
805	7	H	D-1	1		4155	AA	EPA	+
806	7	H	D-1	2		4956	AA	EPA	+
807	7	H	D-5	1		3929	AA	EPA	+
808	7	H	D-5	2		4187	AA	EPA	+
809	7	S	D-3	1		1648	AA	EPA	+
810	7	S	D-3	2		1674	AA	EPA	+
811	41	L	P-1	1		2130	AA	EPA	+
812	41	L	P-1	2		2250	AA	EPA	+

OBS	BA	LEVEL	SAM	REP	CEN	CONC	ANAL	EXTR	CONCAT
813	41	L	P-4	1		2370	AA	EPA	+
814	41	L	P-4	2		1960	AA	EPA	+
815	41	H	P-3	1		43700	AA	EPA	+
816	41	H	P-3	2		42300	AA	EPA	+
817	41	H	P-5	1		41600	AA	EPA	+
818	41	H	P-5	2		40200	AA	EPA	+
819	41	S	P-2	1		130000	AA	EPA	+
820	41	S	P-2	2		129000	AA	EPA	+
821	41	L	D-2	1		99	AA	EPA	+
822	41	L	D-2	2		105	AA	EPA	+
823	41	L	D-4	1		168	AA	EPA	+
824	41	L	D-4	2		97	AA	EPA	+
825	41	H	D-1	1		4920	AA	EPA	+
826	41	H	D-1	2		5450	AA	EPA	+
827	41	H	D-5	1		5180	AA	EPA	+
828	41	H	D-5	2		4970	AA	EPA	+
829	41	S	D-3	1		1280	AA	EPA	+
830	41	S	D-3	2		1300	AA	EPA	+
831	2	L	P-1	1		1773	AA	EPA	+
832	2	L	P-1	2		1669	AA	EPA	+
833	2	L	P-4	1		1576	AA	EPA	+
834	2	L	P-4	2		1522	AA	EPA	+
835	2	H	P-3	1		38312	AA	EPA	+
836	2	H	P-3	2		36048	AA	EPA	+
837	2	H	P-5	1		35498	AA	EPA	+
838	2	H	P-5	2		36621	AA	EPA	+
839	2	S	P-2	1		109414	AA	EPA	+
840	2	S	P-2	2		127416	AA	EPA	+
841	2	L	D-2	1		196	AA	EPA	+
842	2	L	D-2	2		177	AA	EPA	+
843	2	L	D-4	1		97	AA	EPA	+
844	2	L	D-4	2		87	AA	EPA	+
845	2	H	D-1	1		5022	AA	EPA	+
846	2	H	D-1	2		4210	AA	EPA	+
847	2	H	D-5	1		4797	AA	EPA	+
848	2	H	D-5	2		4686	AA	EPA	+
849	2	S	D-3	1		1292	AA	EPA	+
850	2	S	D-3	2		1277	AA	EPA	+

Appendix G-4

Missing/Censored Observations

LEGEND
(Appendix G-4)

OBS = Reported Result

LAB = Laboratory Code

METH = Method Number
- 1 = Microwave/Atomic Absorption Spectrometry
- 2 = Hotplate/Atomic Absorption Spectrometry
- 3 = Microwave/Inductively Coupled Plasma Emission Spectrometry
- 4 = Hotplate/Inductively Coupled Plasma Emission Spectrometry
- 5 = Laboratory X-Ray Fluorescence

EXTR = Extraction Method
- EPA = EPA/AREAL
- NIO = NIOSH Method 7082

ANAL = Analytical Method
- AA = Atomic Absorption Spectrometry
- ICP = Inductively Coupled Plasma Emission Spectrometry
- XRF = Laboratory X-Ray Fluorescence

MTX = Matrix
- P = Paint
- D = Dust

LEVEL = Concentration Level
- L = Low
- H = High
- S = Standard Reference Material (SRM)

CEN = Censored as less than or greater than the concentration reported (µg/g)

CONC = Concentration reported (µg/g)

TRUE = Preliminary calculation of consensus value (without exclusion of outliers)

Missing or censored observations

OBS	LAB	METH	EXTR	ANAL	MTX	LEVEL	CEN	CONC	TRUE
1	38	3	EPA	ICP	P	L			1680
2	46	4	NIO	ICP	P	S			113200
3	30	3	EPA	ICP	P	L	<	10	1680
4	38	3	EPA	ICP	D	L	<	22	100
5	38	3	EPA	ICP	D	L	<	22	100
6	49	4	NIO	ICP	D	L	<	34	100
7	49	4	NIO	ICP	D	L	<	35	100
8	49	4	NIO	ICP	D	L	<	40	100
9	44	4	NIO	ICP	D	L	<	50	100
10	44	4	NIO	ICP	D	L	<	50	100
11	44	4	NIO	ICP	D	L	<	50	100
12	44	4	NIO	ICP	D	L	<	50	100
13	45	4	NIO	ICP	D	L	<	50	100
14	50	5	N/A	XRF	D	L	<	75	100
15	50	5	N/A	XRF	D	L	<	75	100
16	50	5	N/A	XRF	D	L	<	75	100
17	50	5	N/A	XRF	D	L	<	75	100
18	24	2	NIO	AA	D	L	<	100	100
19	41	4	NIO	ICP	D	L	<	100	100
20	41	4	NIO	ICP	D	L	<	100	100
21	48	4	NIO	ICP	D	L	<	200	100
22	48	4	NIO	ICP	D	L	<	200	100
23	48	4	NIO	ICP	D	L	<	200	100
24	48	4	NIO	ICP	D	L	<	200	100
25	28	2	NIO	AA	D	L	<	300	100
26	28	2	NIO	AA	D	L	<	300	100
27	28	2	NIO	AA	D	L	<	300	100
28	28	2	NIO	AA	D	L	<	300	100
29	50	5	N/A	XRF	P	S	>	50000	113200
30	50	5	N/A	XRF	P	S	>	50000	113200

Appendix G-5

Candidate Outlying Observations

LEGEND
(Appendix G-5)

OBS = Reported Result

LAB = Laboratory Code

METH = Method Number
- 1 = Microwave/Atomic Absorption Spectrometry
- 2 = Hotplate/Atomic Absorption Spectrometry
- 3 = Microwave/Inductively Coupled Plasma Emission Spectrometry
- 4 = Hotplate/Inductively Coupled Plasma Emission Spectrometry
- 5 = Laboratory X-Ray Fluorescence

EXTR = Extraction Method
- EPA = EPA/AREAL Method
- NIO = NIOSH Method 7082

ANAL = Analytical Method
- AA = Atomic Absorption Spectrometry
- ICP = Inductively Coupled Plasma Emission Spectrometry
- XRF = Laboratory X-Ray Fluorescence

MTX = Matrix
- P = Paint
- D = Dust

LEVEL = Concentration Level
- L = Low
- H = High
- S = Standard Reference Material (SRM)

TRUE = Preliminary calculation of consensus value (without exclusion of outliers)

CONC = Concentration reported (µg/g)

REC = Calculated recovery - ratio of reported concentration to the nominal concentration

SCOREREC = The recovery score calculated by subtracting the average recovery (method/matrix/level) from the calculated recovery (REC) and dividing by the standard deviation of recovery for a given method/matrix/level

Candidate outlying observations

OBS	LAB	METH	EXTR	ANAL	MTX	LEVEL	TRUE	CONC	REC	SCOREC
1	20	2	NIO	AA	P	S	113200	5077	0.04	-4.12
2	20	2	NIO	AA	P	S	113200	14010	0.12	-3.75
3	14	5	N/A	XRF	D	H	4534	1400	0.31	-3.57
4	33	3	EPA	ICP	D	L	100	31	0.31	-3.43
5	1	3	EPA	ICP	P	H	36611	25000	0.68	-3.38
6	33	3	EPA	ICP	D	H	4534	2500	0.55	-2.79
7	2	2	NIO	AA	D	H	4534	3191	0.70	-2.68
8	15	1	EPA	AA	P	H	36611	22440	0.61	-2.64
9	15	1	EPA	AA	P	H	36611	22640	0.62	-2.61
10	22	2	NIO	AA	P	S	113200	46000	0.41	-2.42
11	1	3	EPA	ICP	P	S	113200	99200	0.88	-2.42
12	25	4	NIO	ICP	D	H	4534	2670	0.59	-2.34
13	25	4	NIO	ICP	P	H	36611	28600	0.78	-2.20
14	4	2	NIO	AA	D	S	1192	960	0.81	-2.19
15	4	2	NIO	AA	D	S	1192	960	0.81	-2.19
16	15	1	EPA	AA	D	H	4534	3929	0.87	-2.14
17	4	2	NIO	AA	P	L	1680	1080	0.64	-2.12
18	17	4	NIO	ICP	P	L	1680	1070	0.64	-2.07
19	17	4	NIO	ICP	P	S	113200	46900	0.41	-2.06
20	2	2	NIO	AA	D	H	4534	3531	0.78	-2.05
21	22	2	NIO	AA	P	S	113200	55000	0.49	-2.05
22	24	3	EPA	ICP	D	H	4534	5640	1.24	2.00
23	21	4	NIO	ICP	D	L	100	160	1.60	2.04
24	25	4	NIO	ICP	D	L	100	160	1.60	2.04
25	3	2	NIO	AA	D	H	4534	5740	1.27	2.05
26	5	1	EPA	AA	P	S	113200	164000	1.45	2.12
27	3	2	NIO	AA	P	H	36611	43600	1.19	2.13
28	23	3	EPA	ICP	D	S	1192	1440	1.21	2.14
29	9	3	EPA	ICP	D	L	100	145	1.45	2.16
30	6	3	EPA	ICP	P	S	113200	135000	1.19	2.20
31	25	3	EPA	ICP	P	L	1680	2120	1.26	2.20
32	19	2	NIO	AA	D	L	100	171	1.71	2.25
33	14	5	N/A	XRF	D	L	100	137	1.37	2.35
34	26	1	EPA	AA	D	L	100	196	1.96	2.45
35	7	4	NIO	ICP	P	H	36611	44340	1.21	2.52
36	23	3	EPA	ICP	D	S	1192	1490	1.25	2.54
37	23	3	EPA	ICP	P	H	36611	46300	1.26	2.62
38	1	4	NIO	ICP	P	L	1680	2330	1.39	2.69
39	3	2	NIO	AA	P	H	36611	46300	1.26	3.03
40	20	2	NIO	AA	D	L	100	199	1.99	3.29
41	21	3	EPA	ICP	D	L	100	170	1.70	3.38
42	1	4	NIO	ICP	D	S	1192	1830	1.54	3.39
43	7	4	NIO	ICP	P	H	36611	47300	1.29	3.40
44	1	4	NIO	ICP	D	H	4534	7150	1.58	3.50
45	20	2	NIO	AA	D	L	100	214	2.14	3.84
46	21	4	NIO	ICP	D	L	100	270	2.70	5.22
47	27	3	EPA	ICP	D	L	100	211	2.11	5.40
48	15	1	EPA	AA	D	L	100	451	4.51	10.62
49	15	1	EPA	AA	D	L	100	465	4.65	11.07
50	15	1	EPA	AA	D	L	100	539	5.39	13.44
51	15	1	EPA	AA	D	L	100	567	5.67	14.34
52	14	5	N/A	XRF	P	L	1680	5148	3.06	23.44
53	14	5	N/A	XRF	P	L	1680	5434	3.23	25.07
	14	5	N/A	XRF	P	L	1680	5823	3.47	27.28
	14	5	N/A	XRF	P	L	1680	6003	3.57	28.31

Appendix G-6

Method Means, Consensus Values, Repeatability and Reproducibility

Results of Statistical Analysis

MTX	LEVEL	METH	SW	SB	STOT	MEAN	L95	U95	TRUE	LT95	UT95	N	NO	K	KO
D	H	1	296	301	422	4847	4599	5095	4550	4316	4785	28	28	7	7
D	H	2	441	214	491	4677	4475	4879	4550	4316	4785	35	36	9	9
D	H	3	501	226	549	4281	4059	4503	4550	4316	4785	35	36	9	9
D	H	4	574	311	653	4397	4136	4657	4550	4316	4785	41	42	10	10
D	H	5	98	305	320	2485	2257	2714	4550	4316	4785	27	28	7	7
D	L	1	23	8	25	114	102	125	104	91	117	23	28	6	7
D	L	2	14	17	23	108	95	121	104	91	117	29	36	8	9
D	L	3	17	0	17	98	92	104	104	91	117	31	36	9	9
D	L	4	23	25	34	98	79	116	104	91	117	27	42	9	10
D	L	5	8	20	22	93	77	109	104	91	117	24	28	6	7
D	S	1	38	188	192	1327	1186	1468	1186	1096	1277	14	14	7	7
D	S	2	45	89	100	1173	1111	1235	1186	1096	1277	18	18	9	9
D	S	3	55	60	82	1133	1086	1180	1186	1096	1277	18	18	9	9
D	S	4	36	129	134	1112	1031	1194	1186	1096	1277	20	21	10	10
D	S	5	24	84	88	1029	965	1093	1186	1096	1277	14	14	7	7
P	H	1	2386	3150	3951	41281	38780	43782	37632	35872	39391	26	28	7	7
P	H	2	1860	1920	2674	36921	35523	38318	37632	35872	39391	35	36	9	9
P	H	3	1445	1880	2372	36654	35336	37972	37632	35872	39391	35	36	9	9
P	H	4	1708	2377	2927	35670	34109	37231	37632	35872	39391	41	42	10	10
P	H	5	984	4118	4234	27404	24332	30476	37632	35872	39391	28	28	7	7
P	L	1	217	128	252	1896	1772	2020	1690	1567	1814	28	28	7	7
P	L	2	200	197	281	1661	1517	1806	1690	1567	1814	36	36	9	9
P	L	3	196	91	216	1603	1514	1692	1690	1567	1814	34	36	9	9
P	L	4	154	196	249	1600	1470	1730	1690	1567	1814	41	42	10	10
P	L	5	34	185	188	1034	885	1182	1690	1567	1814	24	28	6	7
P	S	1	8829	16043	18312	122432	109679	135185	109859	96964	122753	14	14	7	7
P	S	2	5934	24194	24911	104340	87325	121356	109859	96964	122753	16	18	8	9
P	S	3	5159	6469	8274	118281	113429	123133	109859	96964	122753	18	18	9	9
P	S	4	11239	20789	23633	94382	80620	108143	109859	96964	122753	20	21	10	10
P	S	5	1582	32457	32496	112721	86735	138708	109859	96964	122753	12	14	6	7

LEGEND

MTX =	Matrix (D=Dust; P=Paint)
Level =	H=High; L=Low; S=SRM
Meth =	Method (1=MW/AAS; 2=HP/AAS; 3=MW/ICP; 4=HP/ICP; 5=Lab XRF)
SW =	Repeatability (within-lab standard deviation)
STOT =	Reproducibility (within-lab and between-lab standard deviation)
SB =	Pure between-lab standard deviation
MEAN =	Method Mean
L95, U95 =	Lower and Upper Limits of 95% Confidence Interval of the Method Mean
TRUE =	Consensus Value (average of means of methods 1 through 4)
LT95, UT95 =	Lower and Upper Limits of 95% Confidence Interval of Consensus Value
N =	Total sample size
NO =	Expected sample size
K =	Number of labs for nonmissing, noncensored, and nonoutlying data
K =	Expected number of labs

Appendix G-7

Recovery and Log of Recovery Plots by Laboratory

LEGEND

(Appendix G-7)

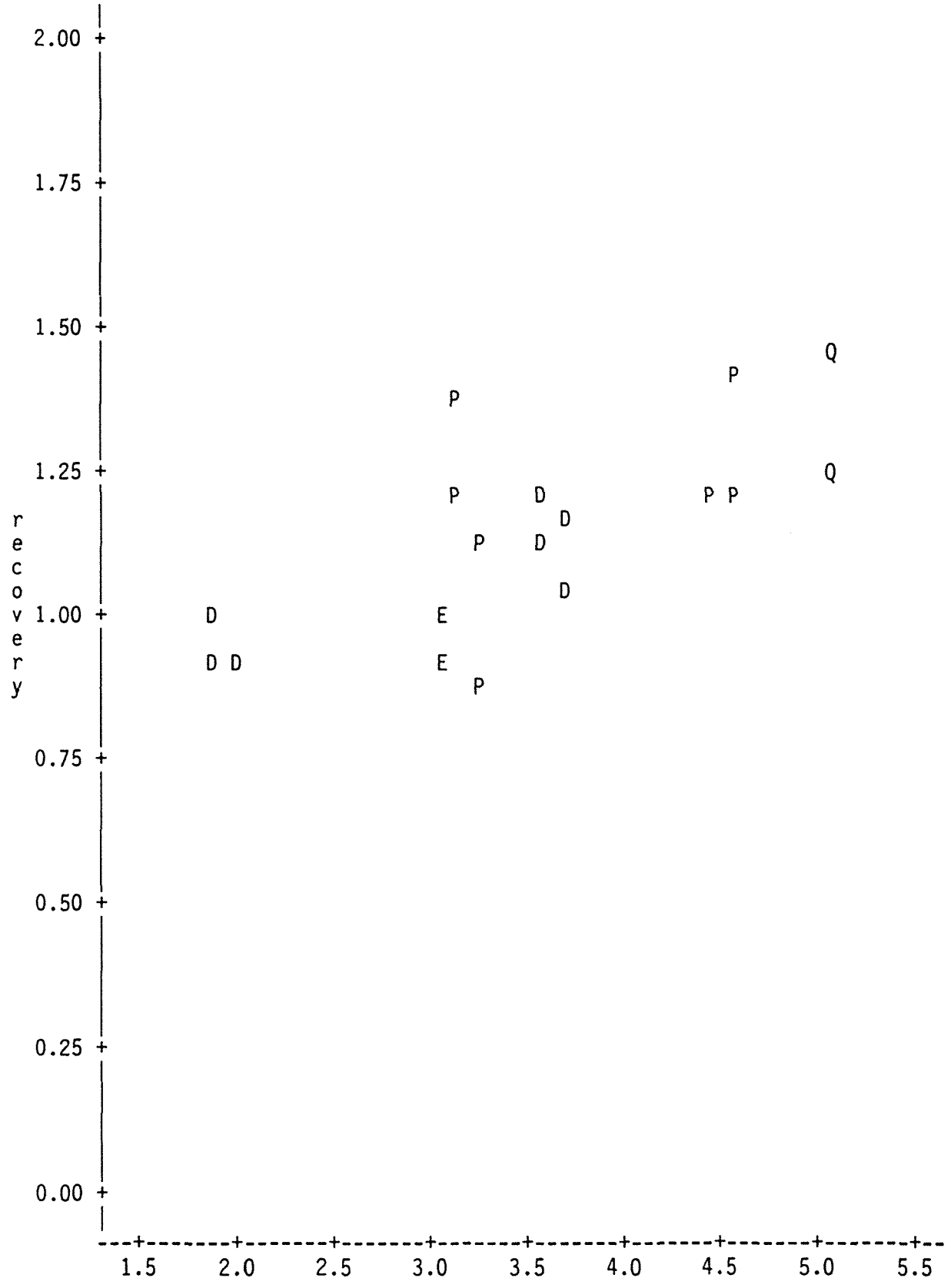
D = Dust (low dust and high dust)
E = "Dust" SRM 2711
P = Paint (low paint and high paint)
Q = Paint SRM 1579

Appendix G-7-1

MW/AAS Laboratories

---------- METH=1 LAB=10 ----------

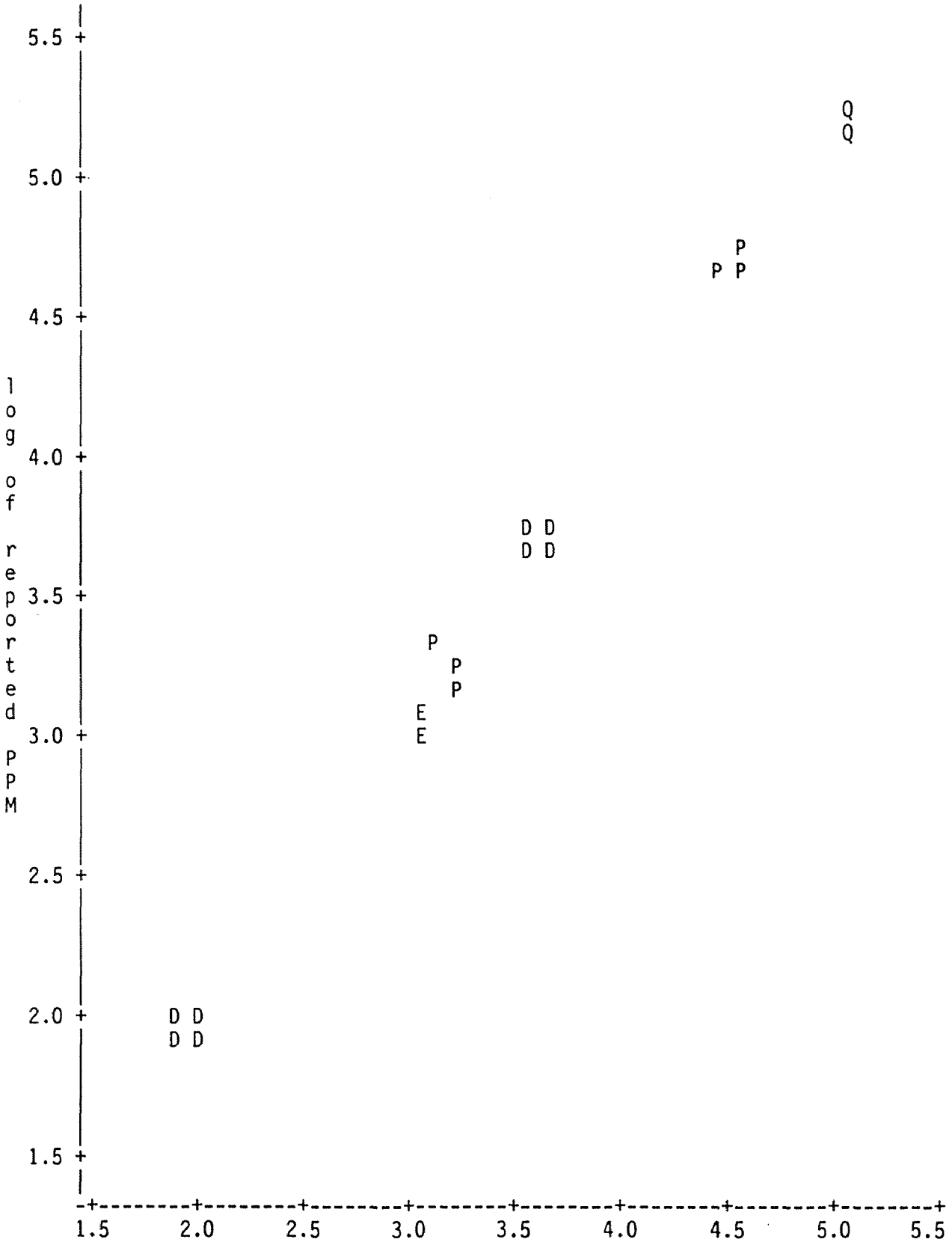
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 2 obs hidden.

---------- METH=1 LAB=10 ----------

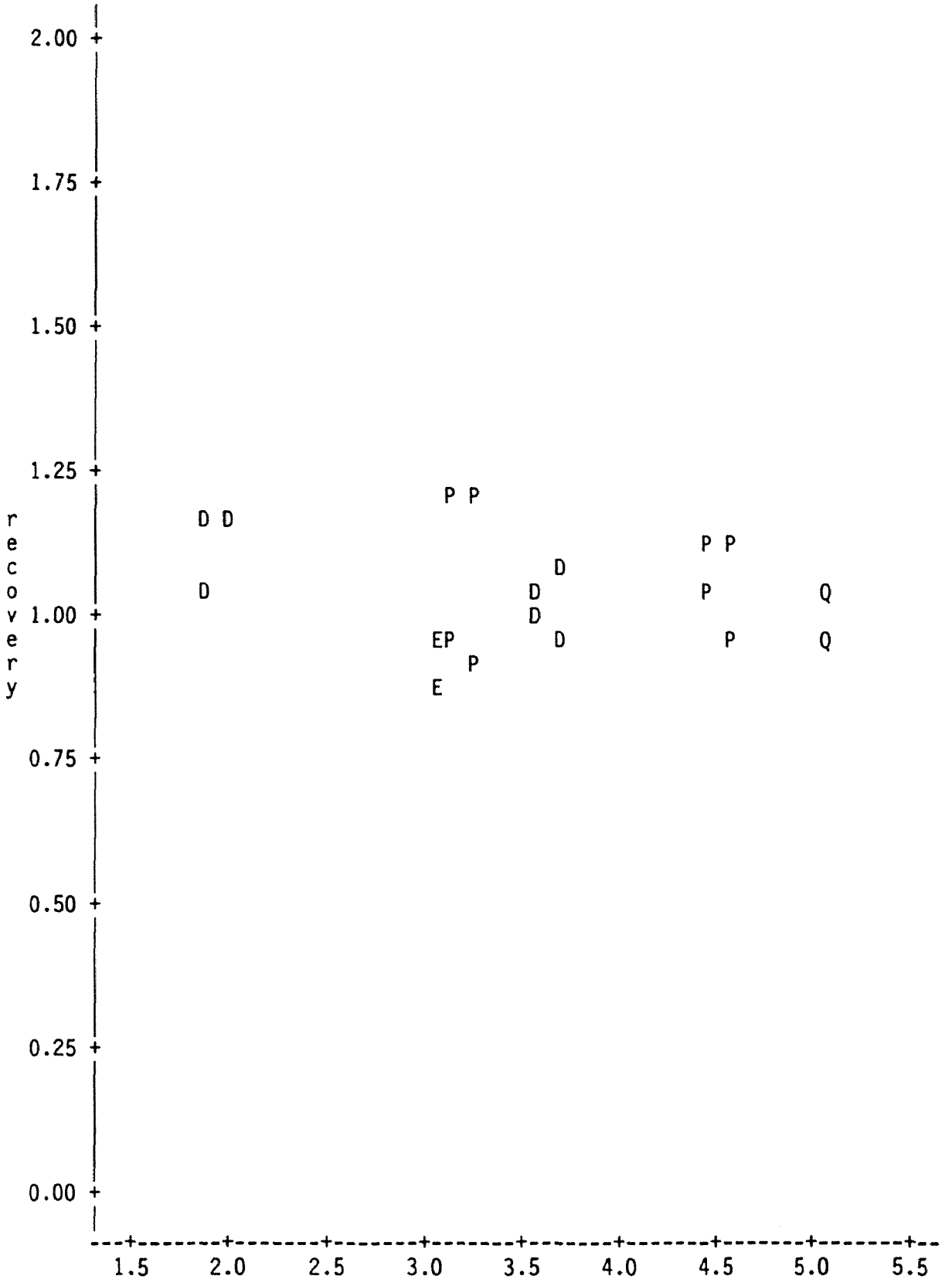
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 2 obs hidden.

---------- METH=1 LAB=11 ----------

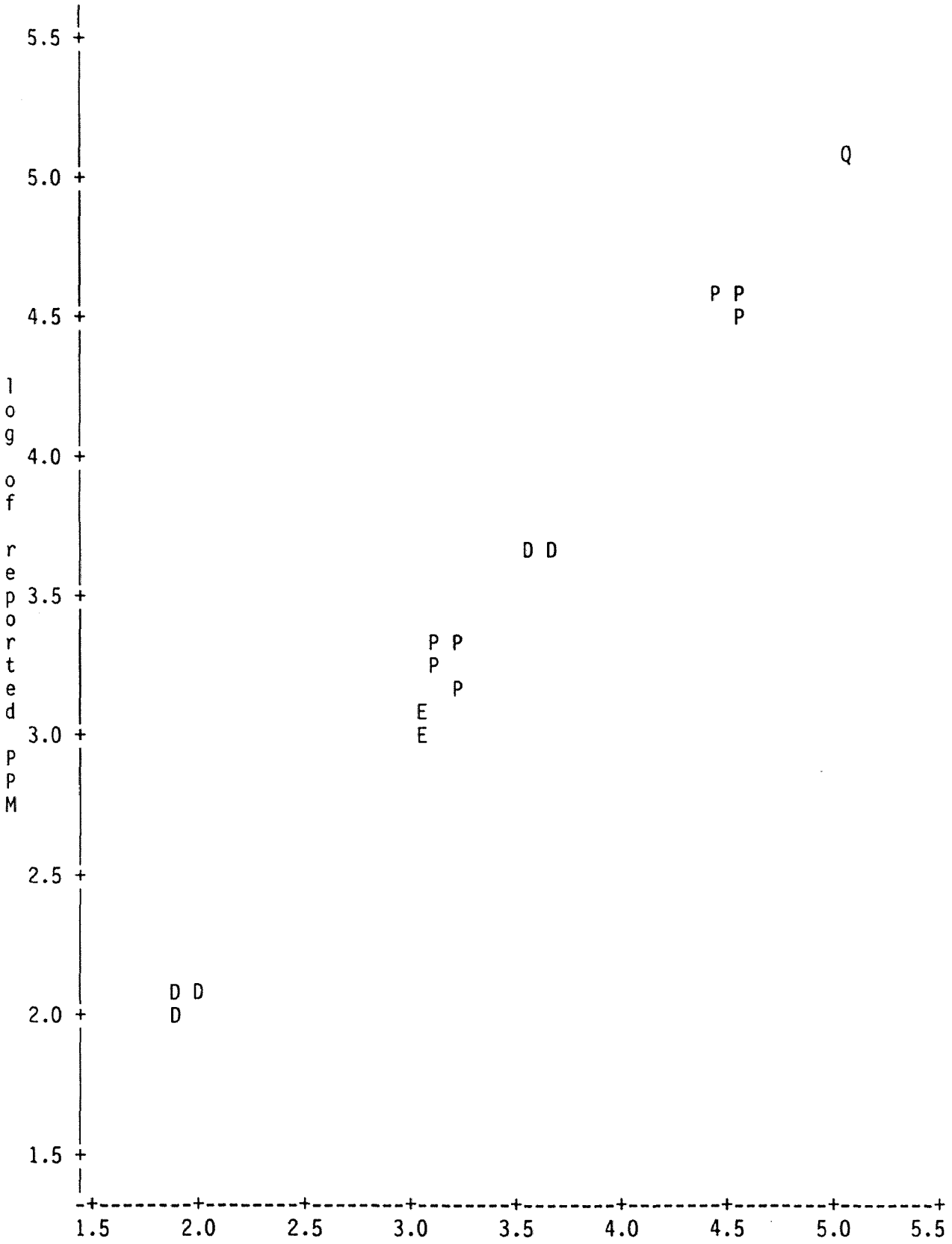
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 1 obs hidden.

---------- METH=1 LAB=11 ----------

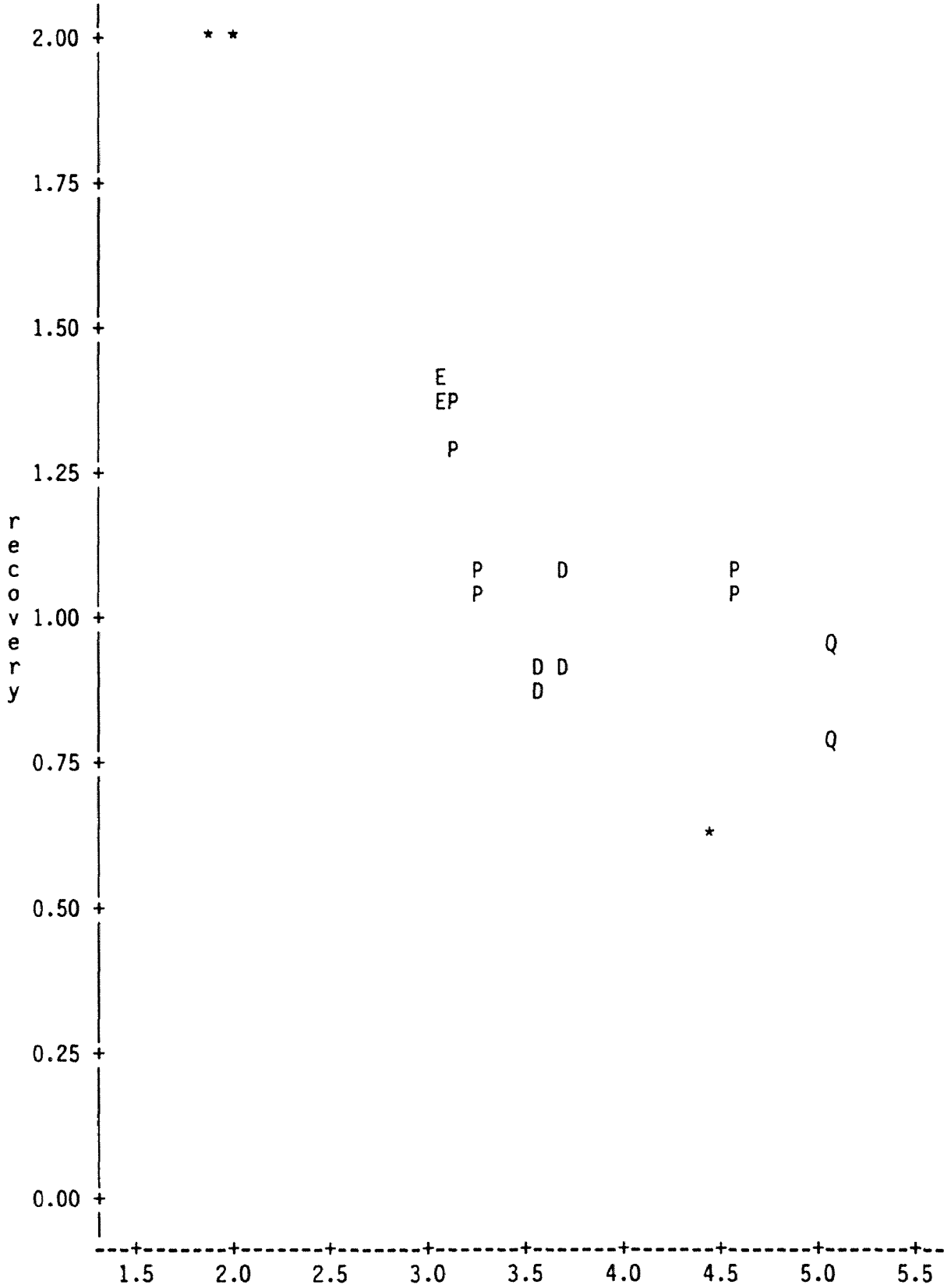
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 5 obs hidden.

---------- METH=1 LAB=12 ----------

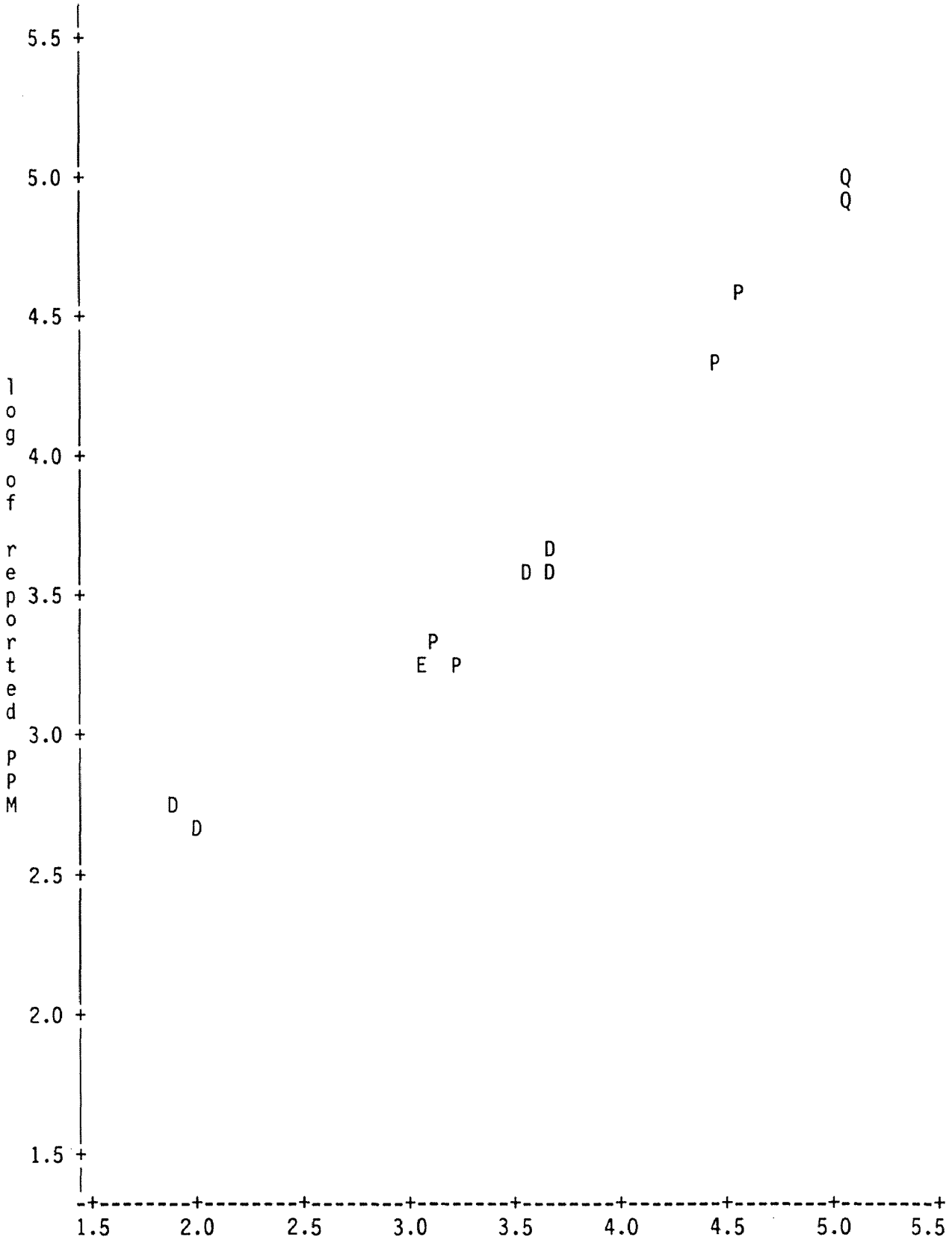
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 3 obs hidden.

---------- METH=1 LAB=12 ----------

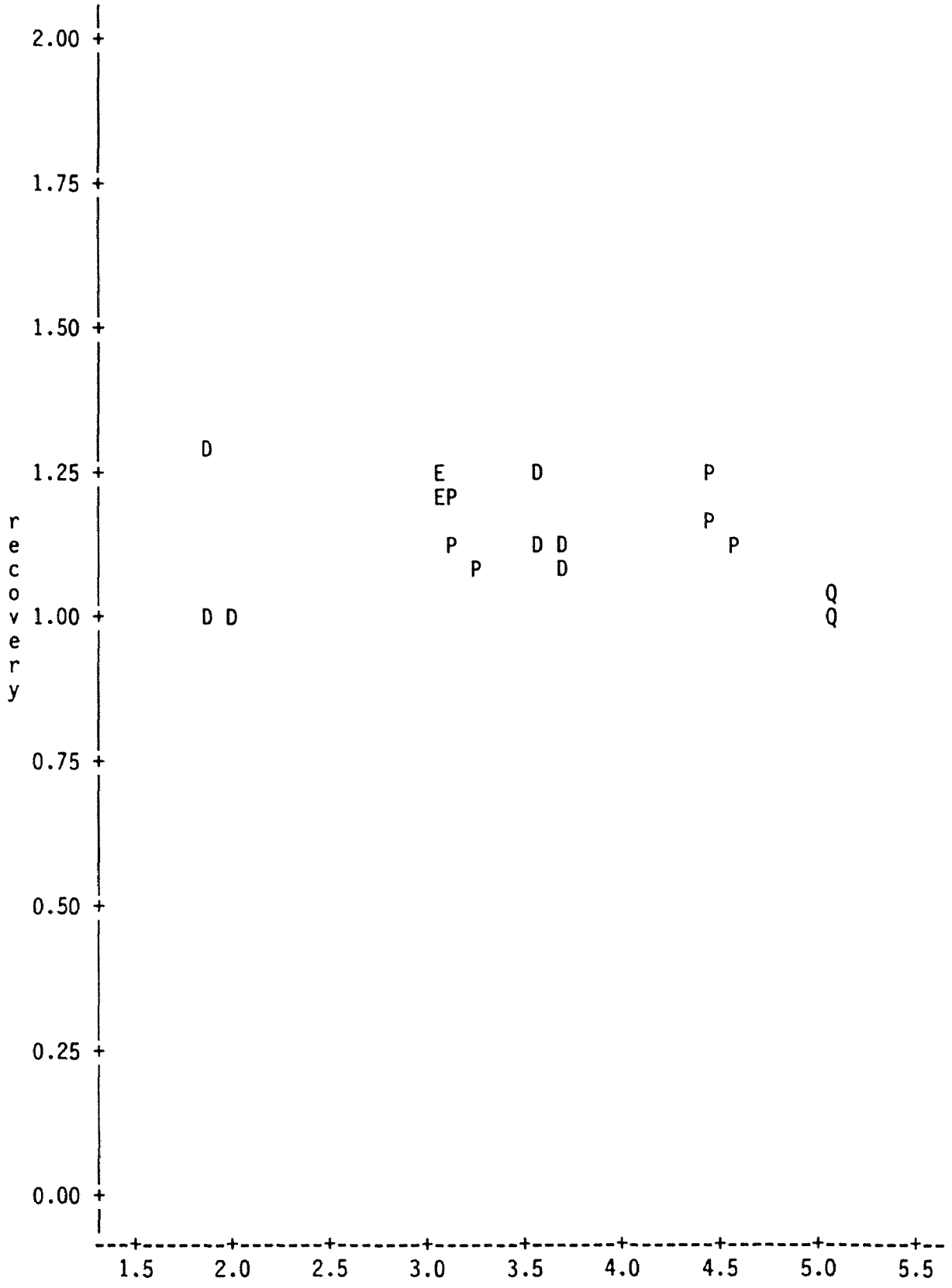
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 8 obs hidden.

---------- METH=1 LAB=13 ----------

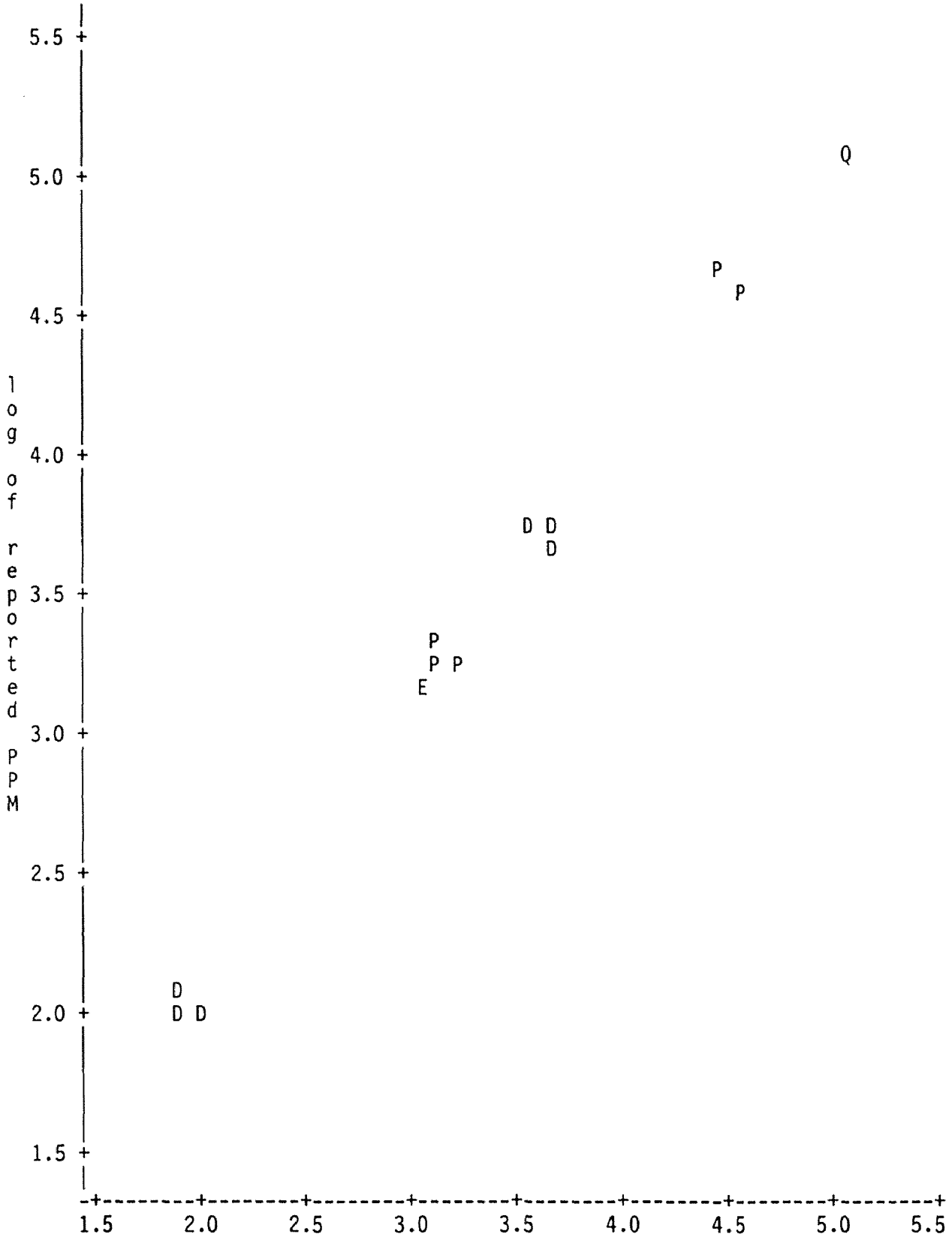
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 3 obs hidden.

---------- METH=1 LAB=13 ----------

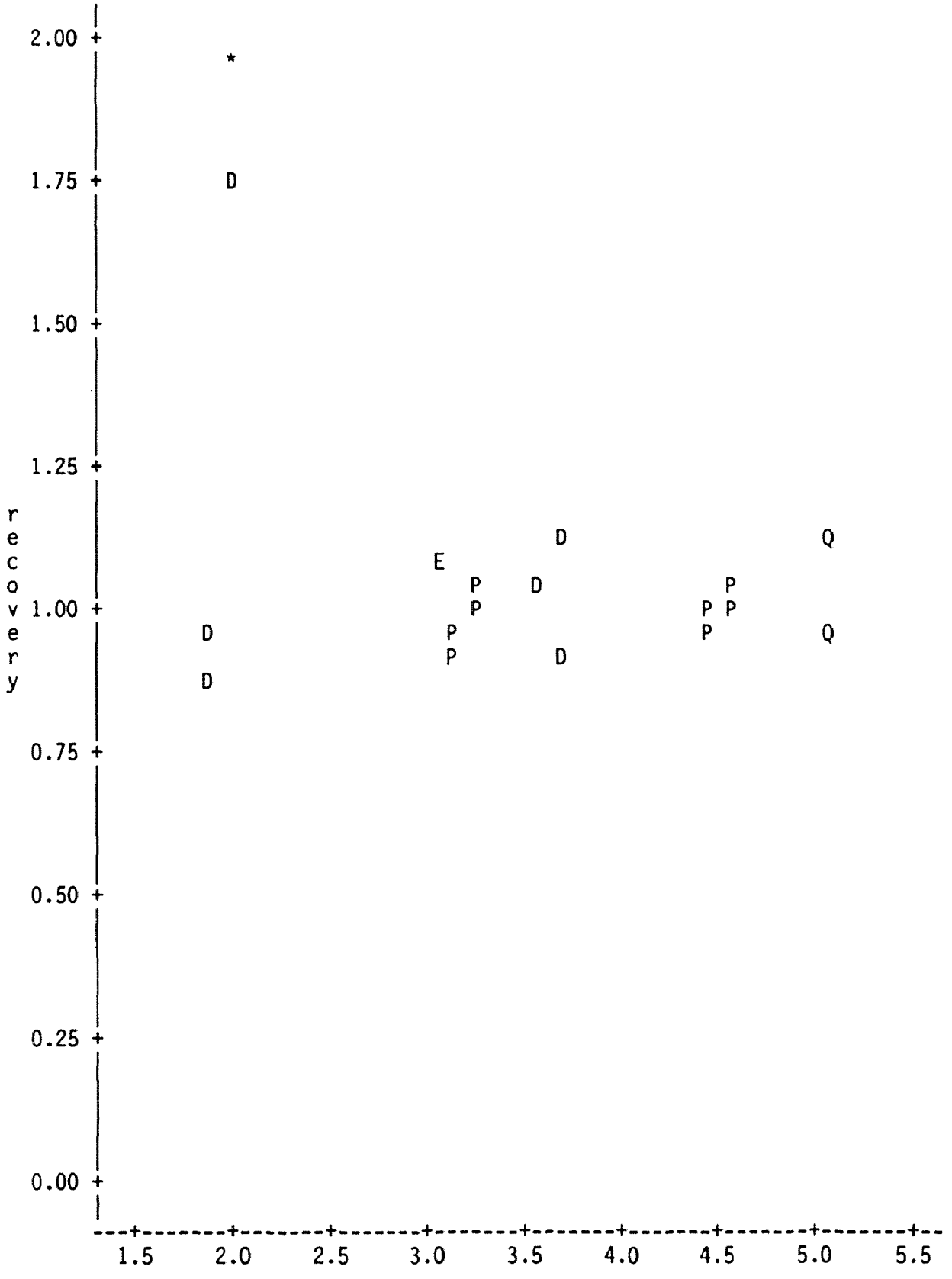
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 7 obs hidden.

---------- METH=1 LAB=14 ----------

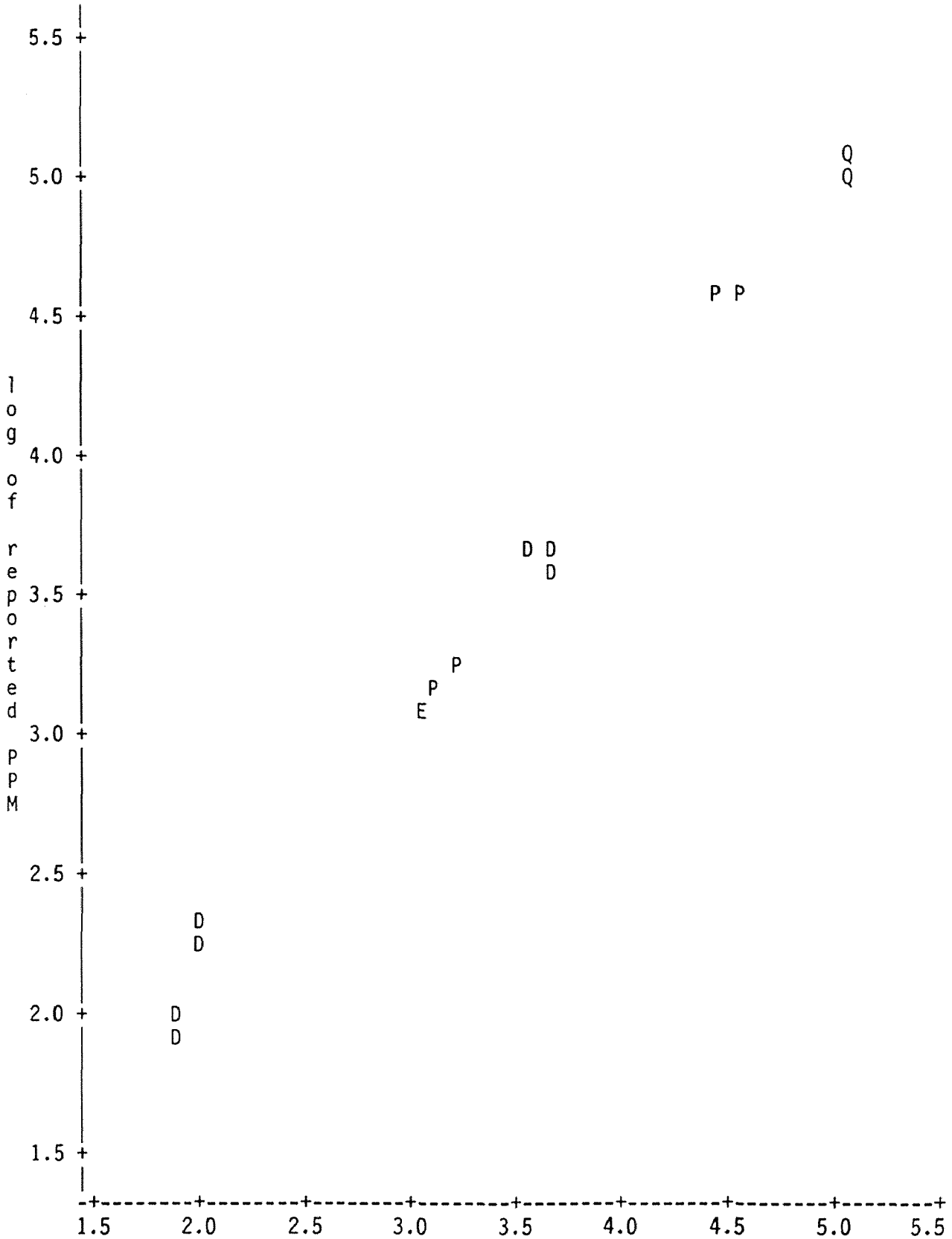
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 2 obs hidden.

---------- METH=1 LAB=14 ----------

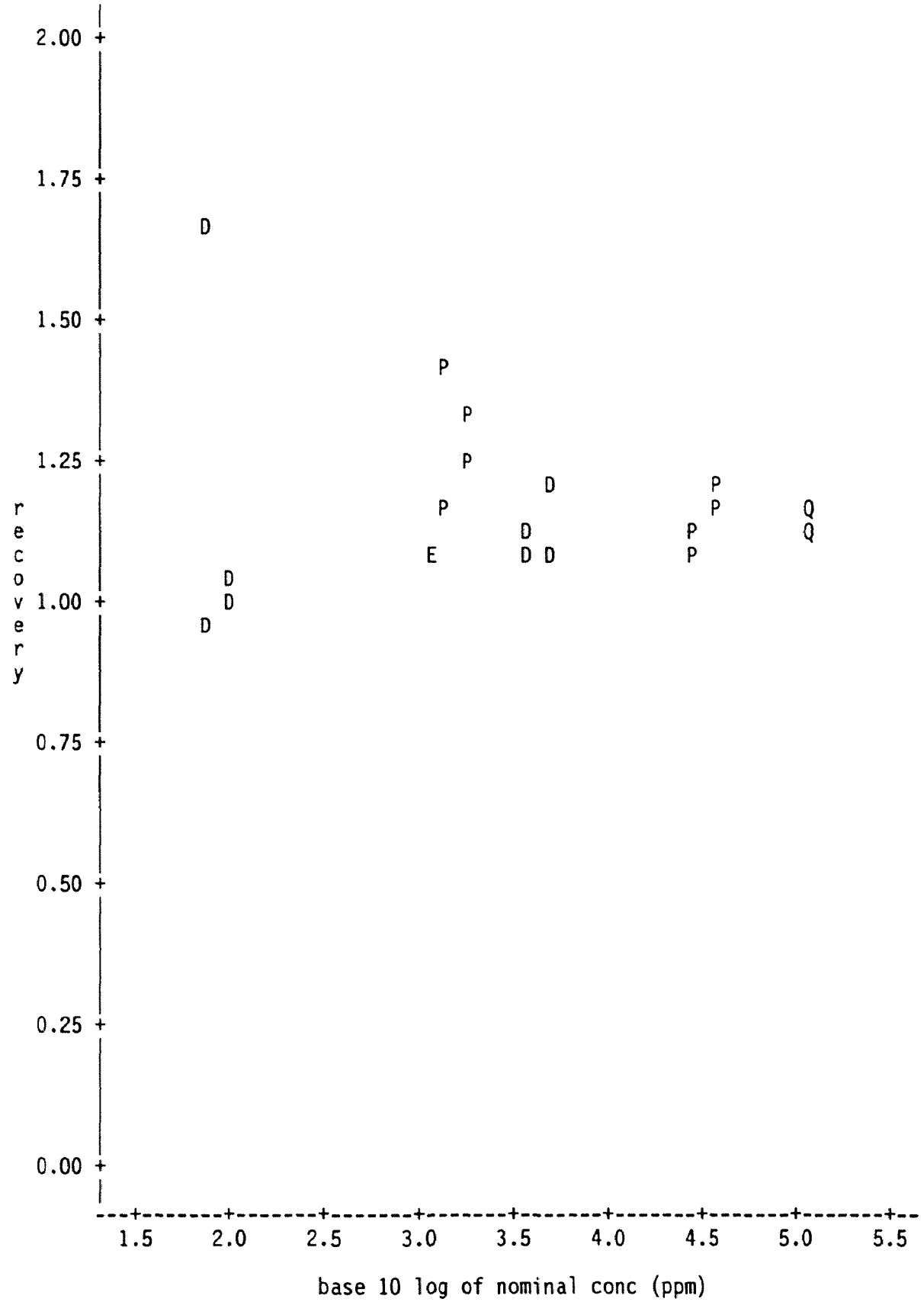
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 6 obs hidden.

---------- METH=1 LAB=15 ----------

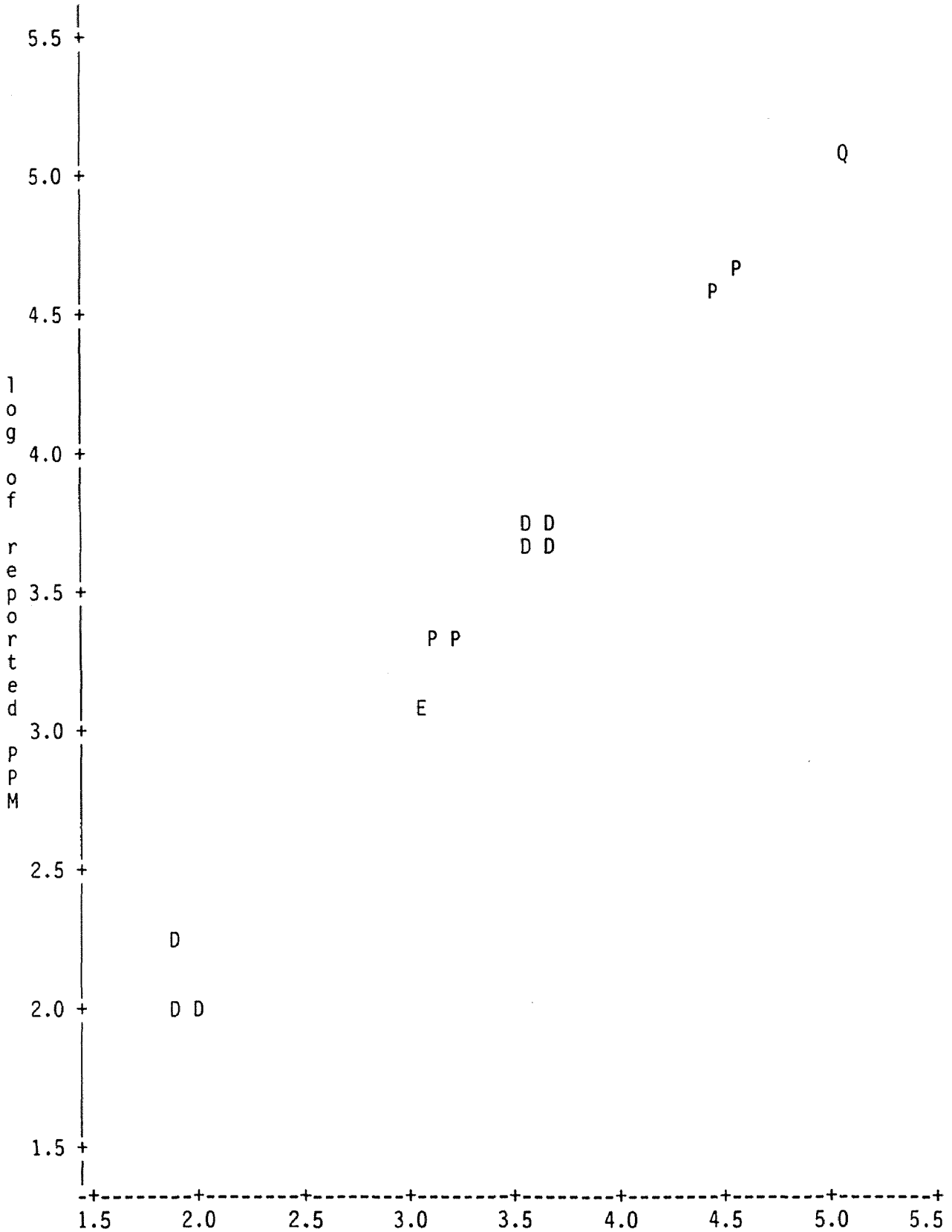
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 1 obs hidden.

---------- METH=1 LAB=15 ----------

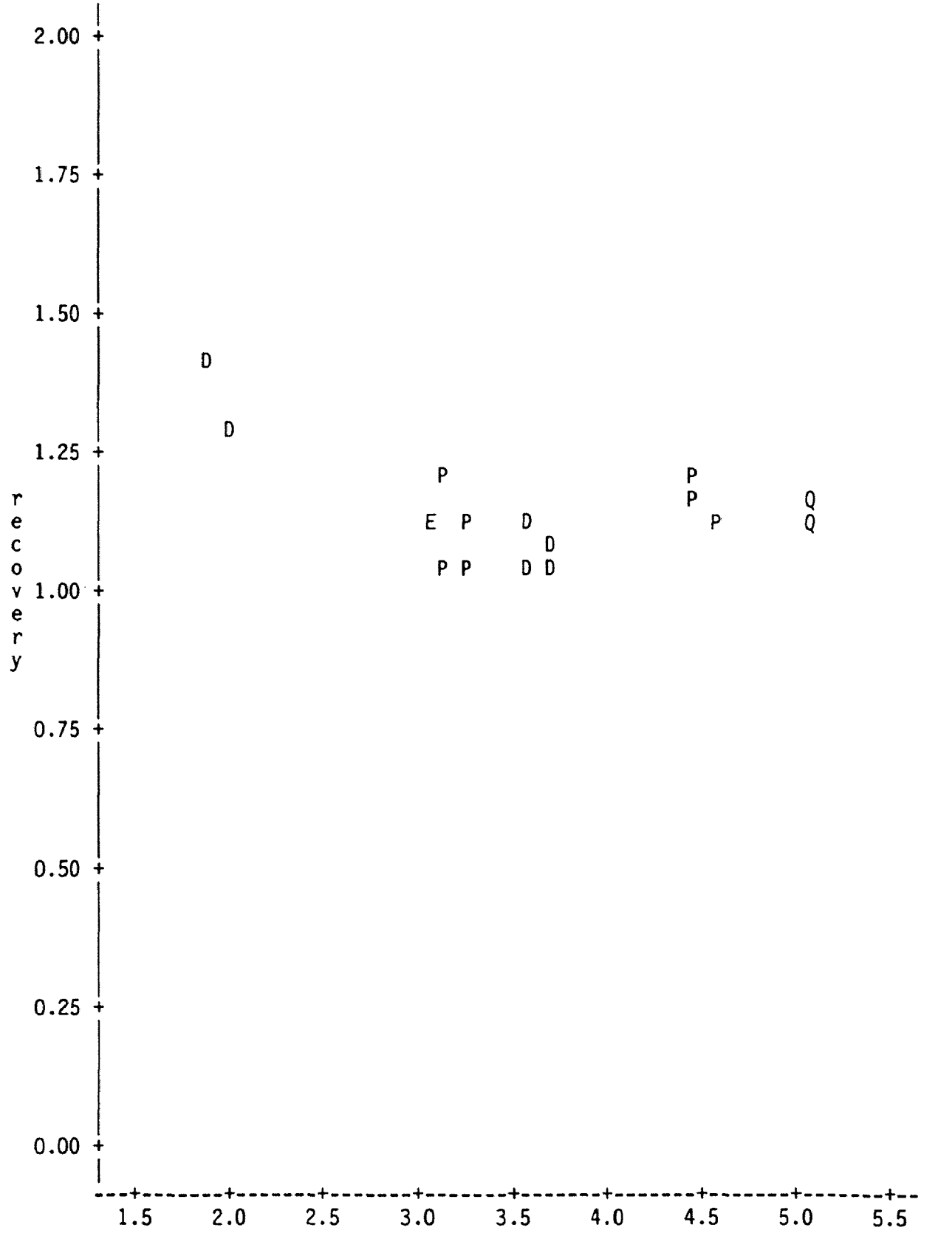
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 7 obs hidden.

---------- METH=1 LAB=16 ----------

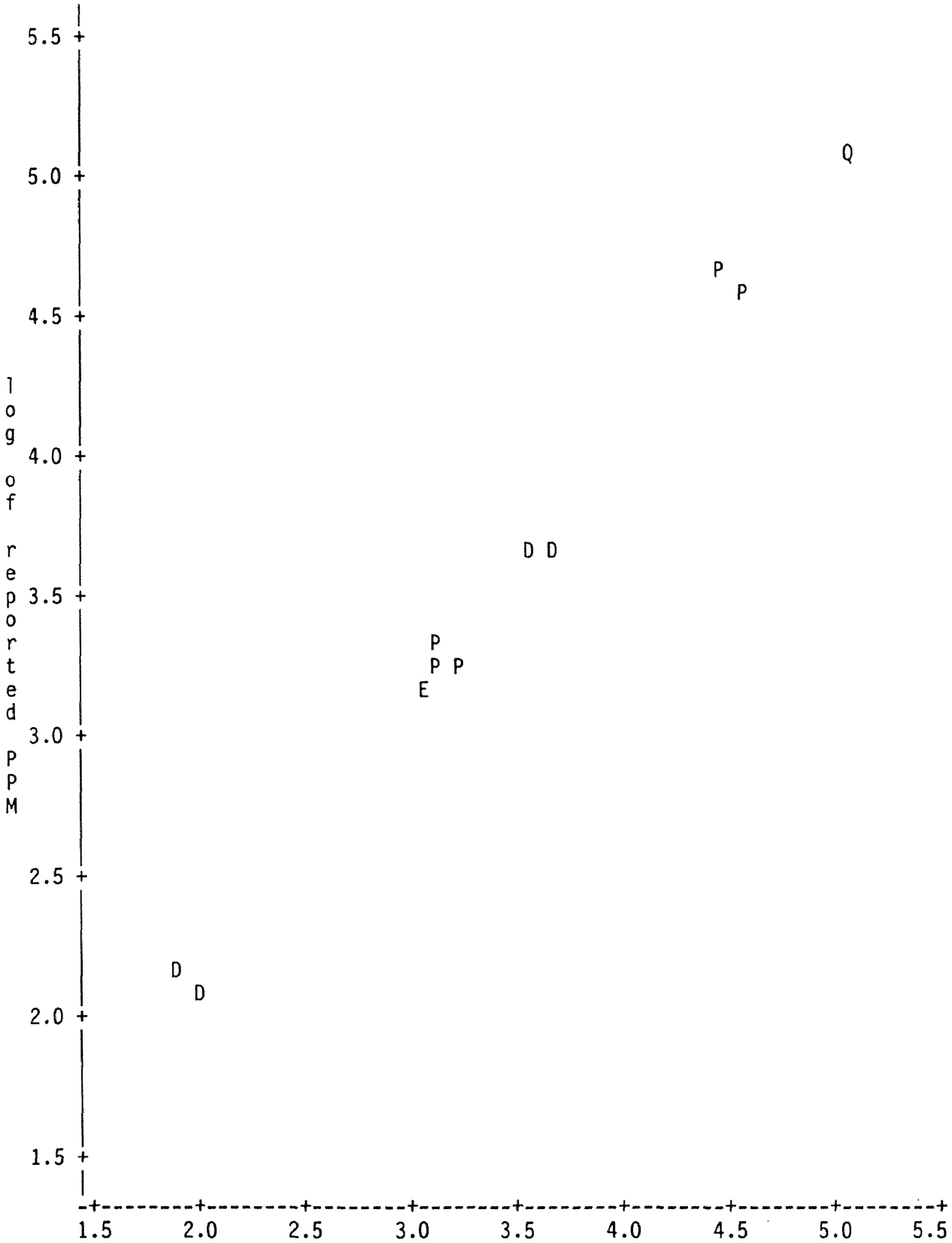
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 4 obs hidden.

---------- METH=1 LAB=16 ----------

Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



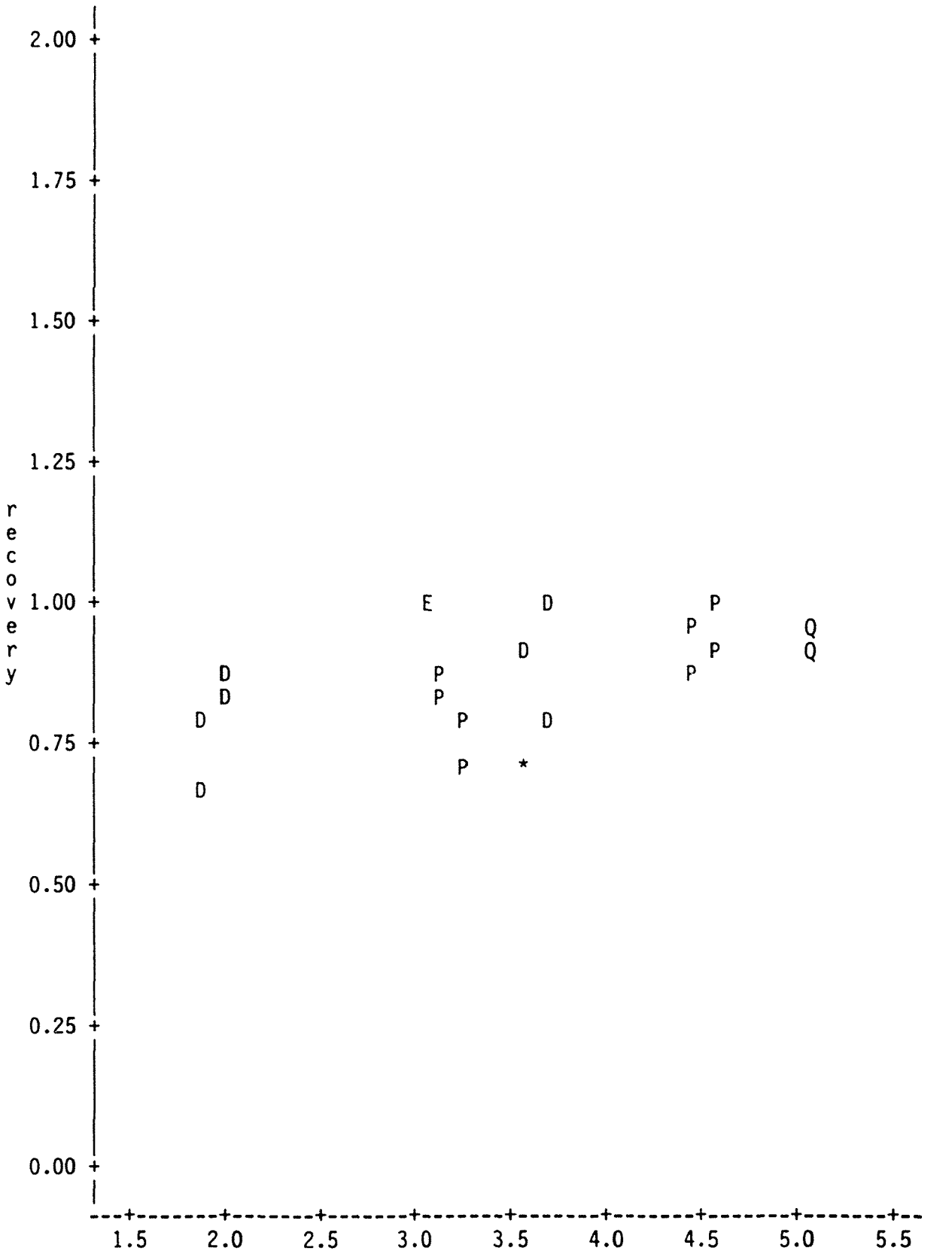
NOTE: 9 obs hidden.

Appendix G-7-2

HP/AAS Laboratories

---------- METH=2 LAB=20 ----------

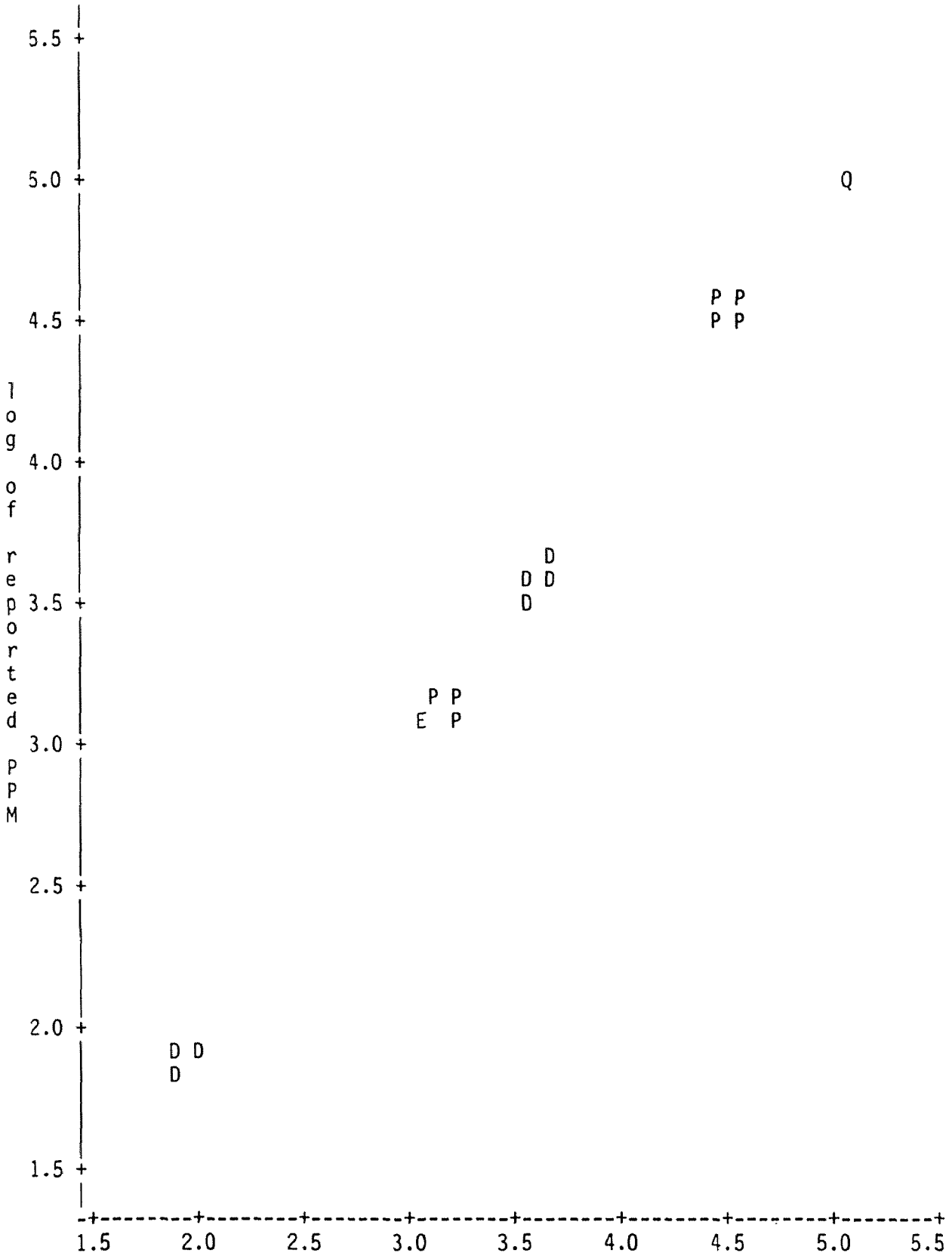
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 1 obs hidden.

---------- METH=2 LAB=20 ----------

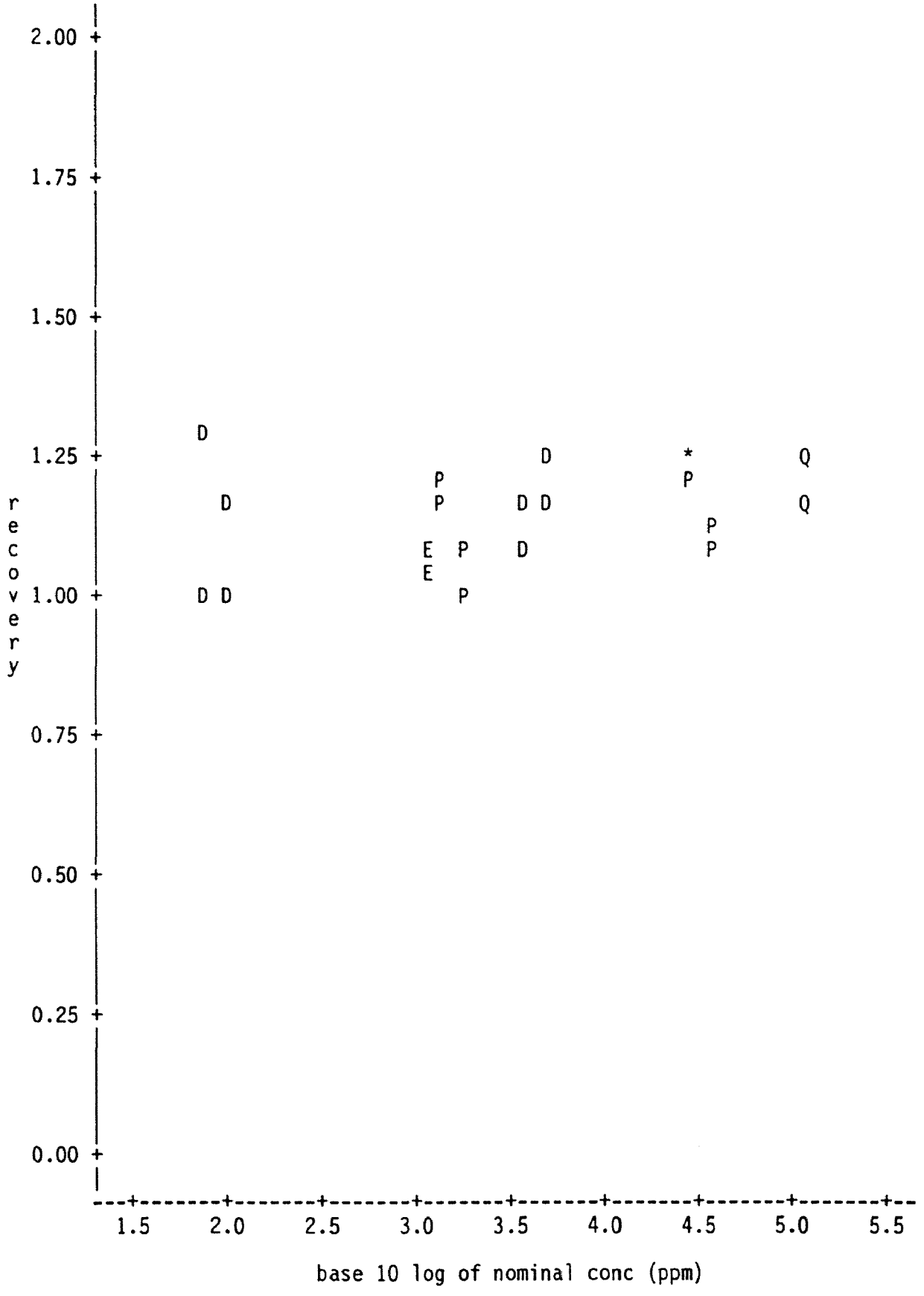
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 4 obs hidden.

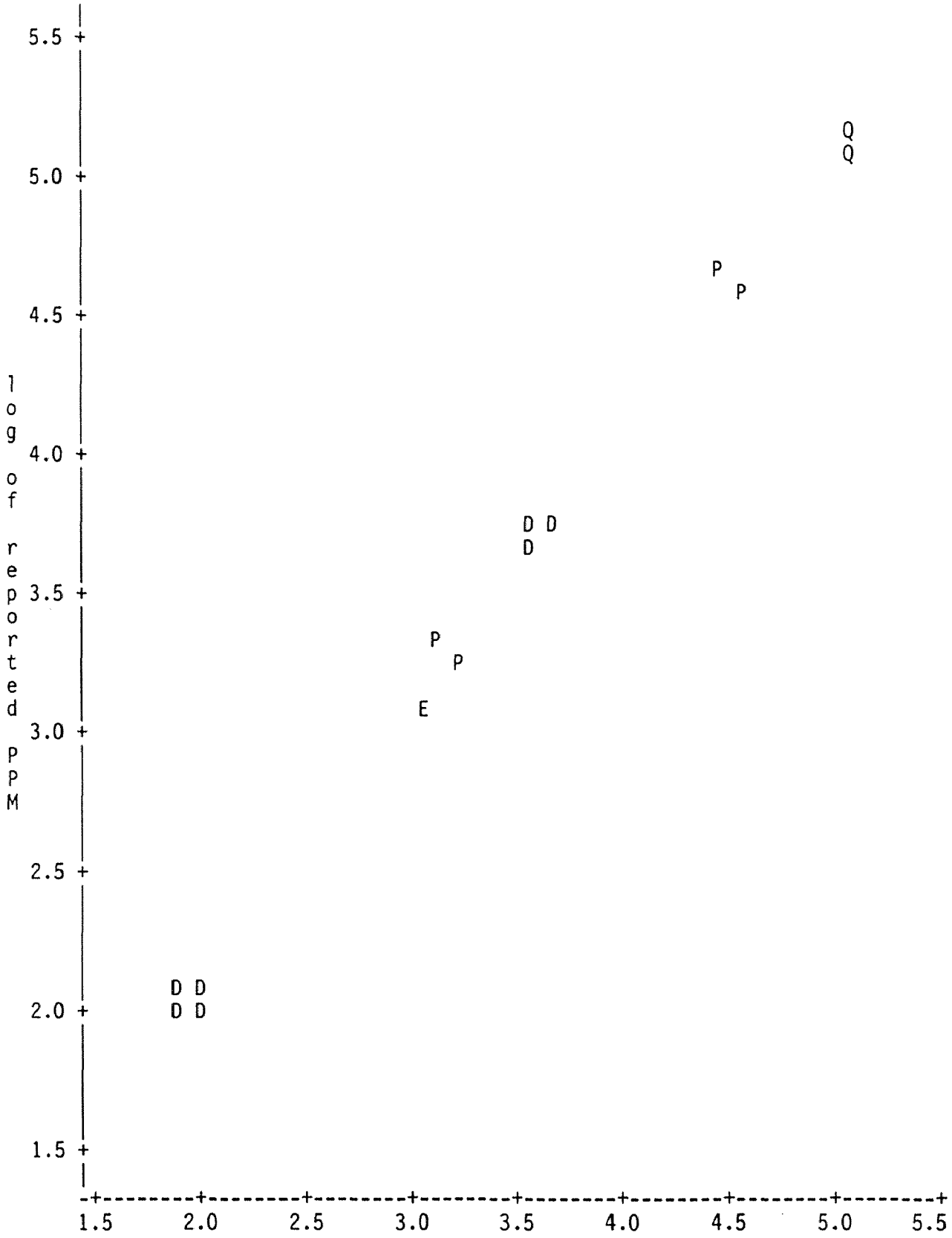
---------- METH=2 LAB=21 ----------

Plot of REC*LOGTRUE. Symbol is value of MTX.



---------- METH=2 LAB=21 ----------

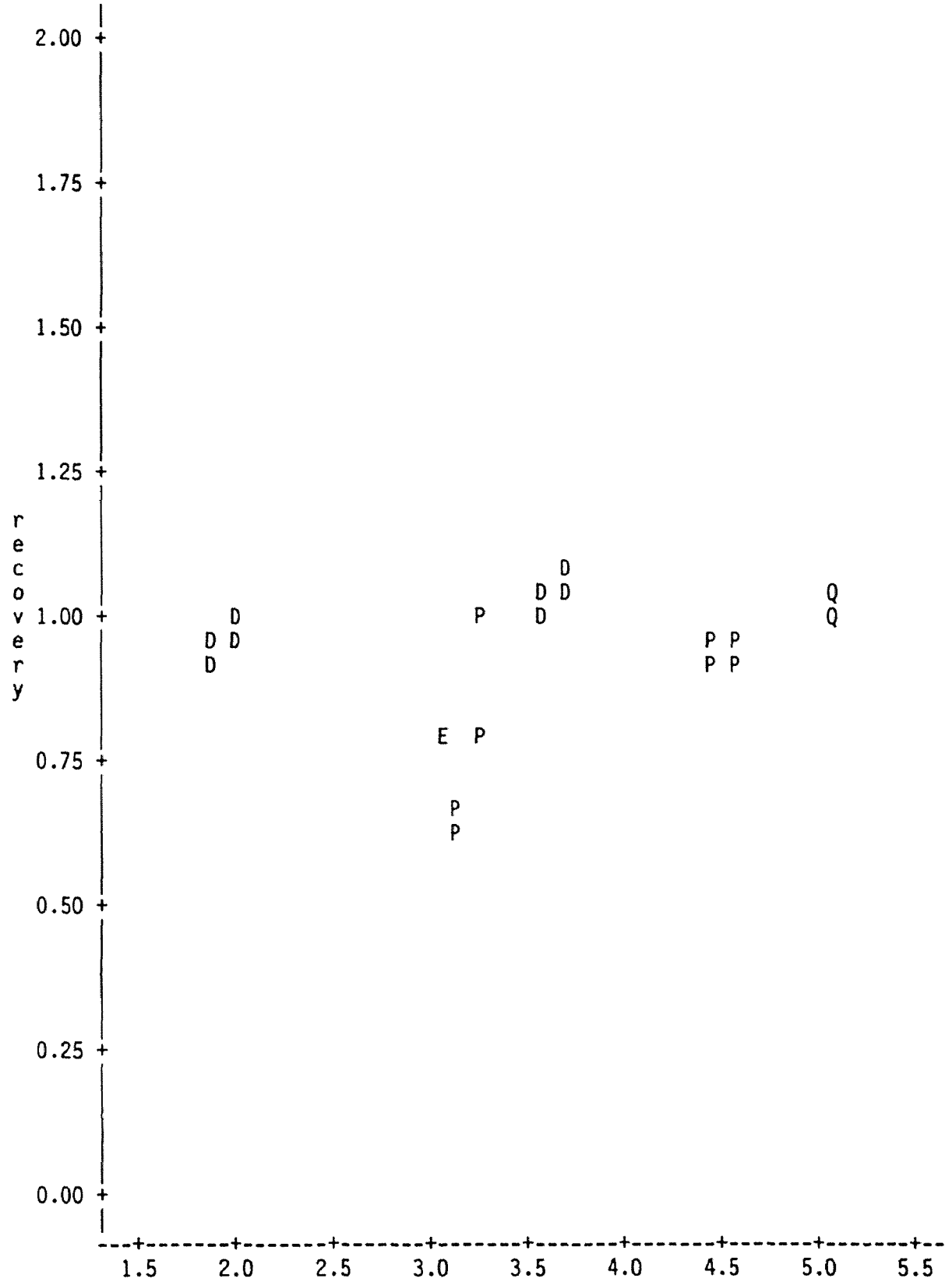
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 6 obs hidden.

---------- METH=2 LAB=22 ----------

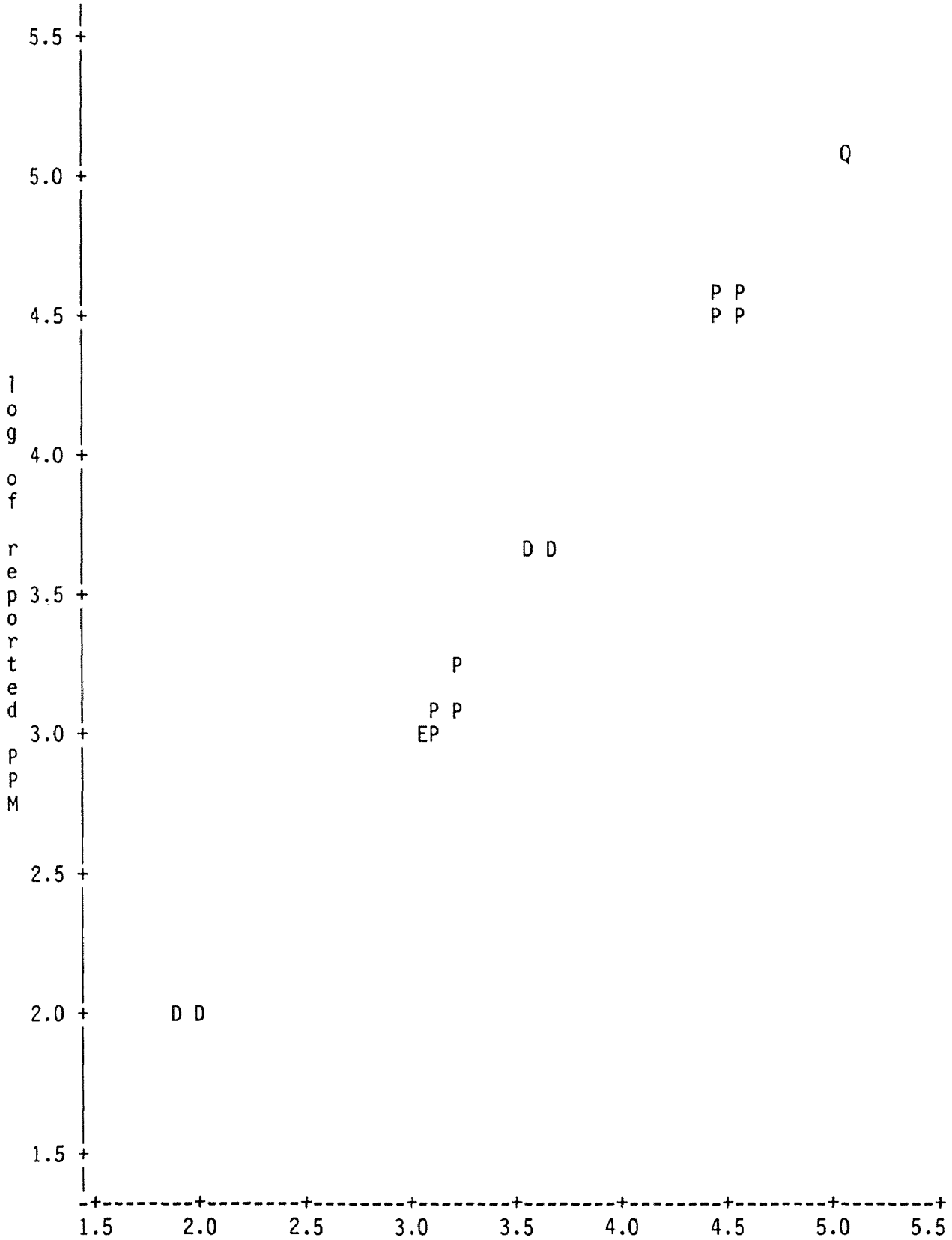
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 1 obs hidden.

---------- METH=2 LAB=22 ----------

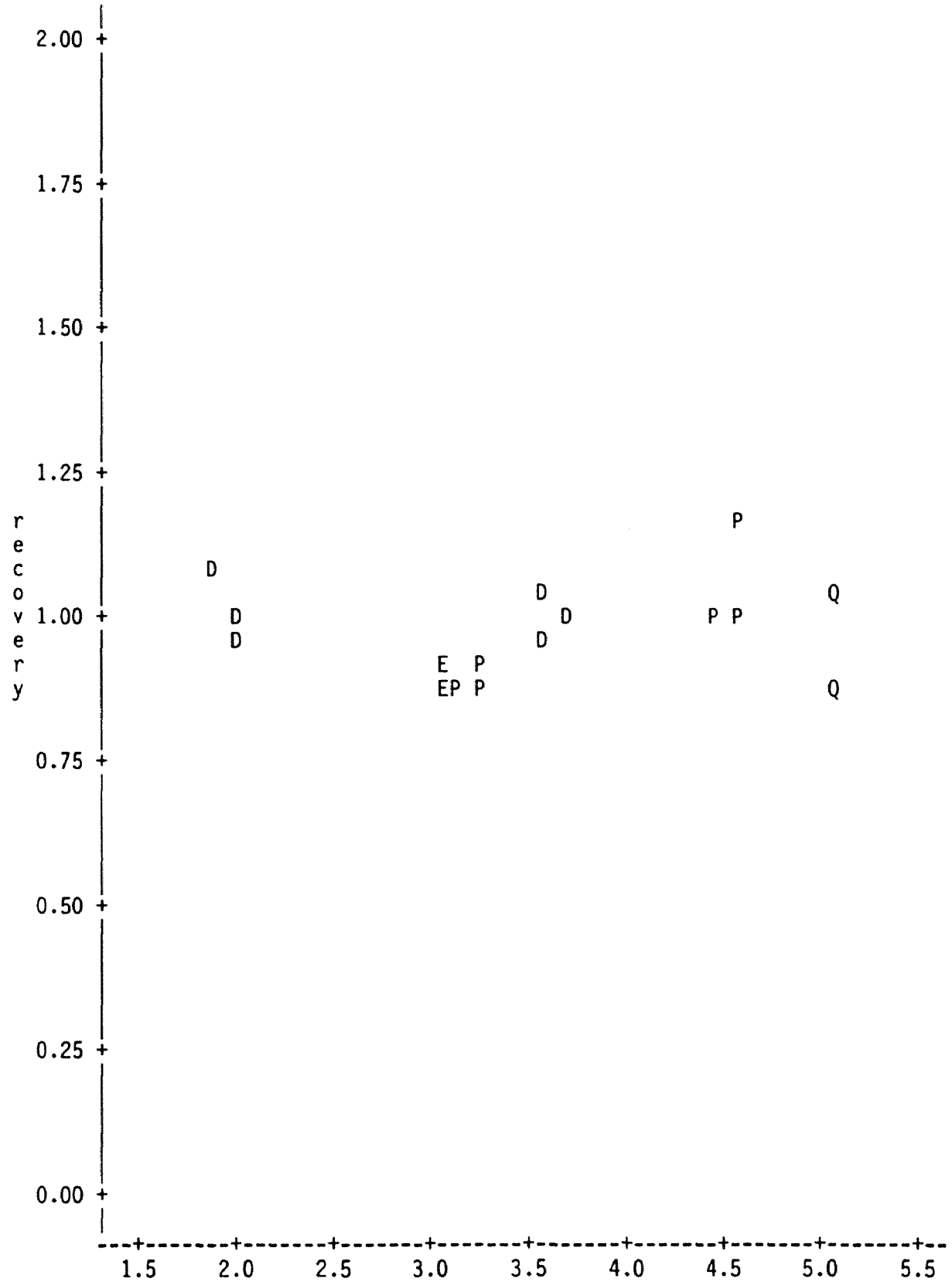
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 6 obs hidden.

---------- METH=2 LAB=23 ----------

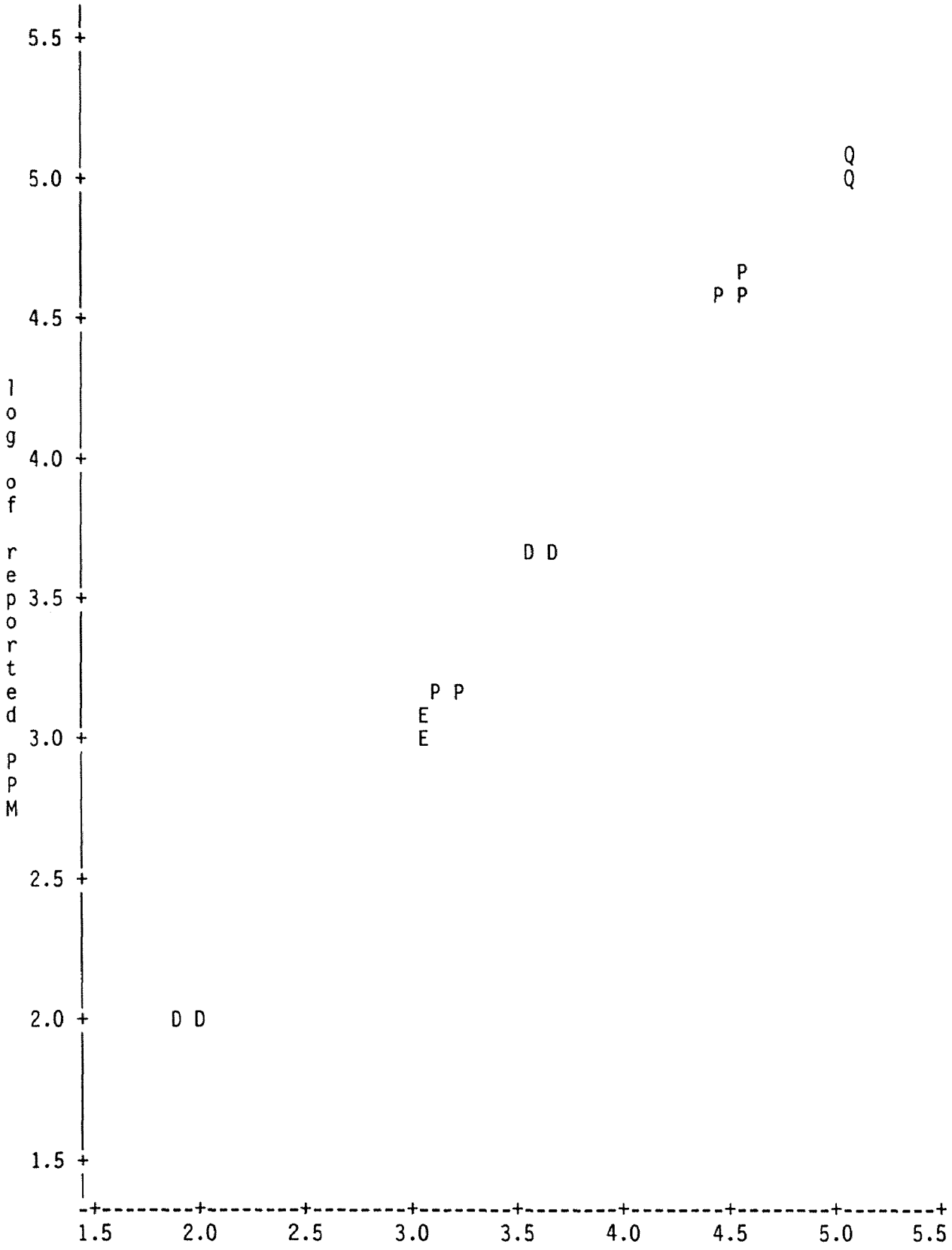
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 4 obs hidden.

---------- METH=2 LAB=23 ----------

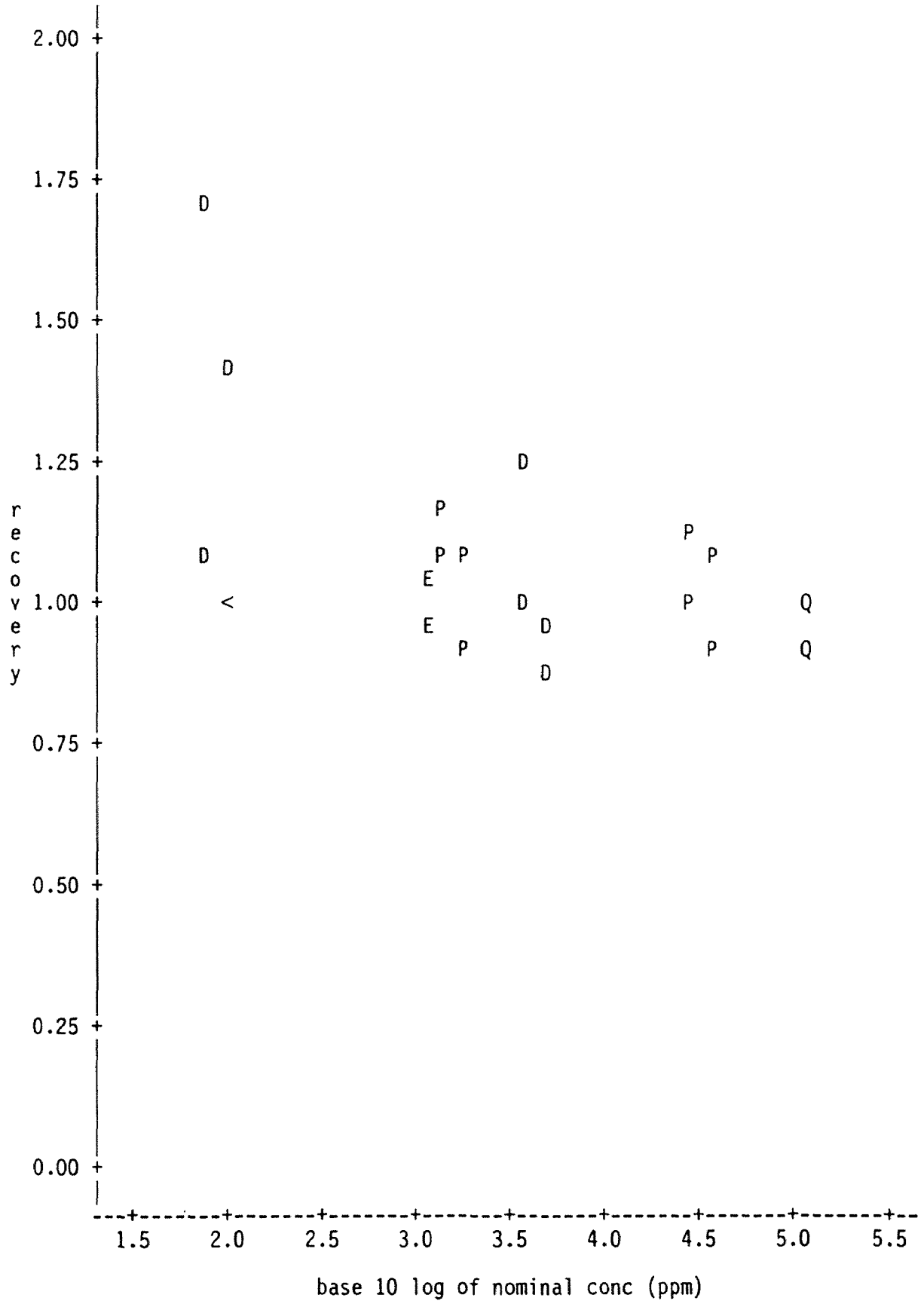
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 7 obs hidden.

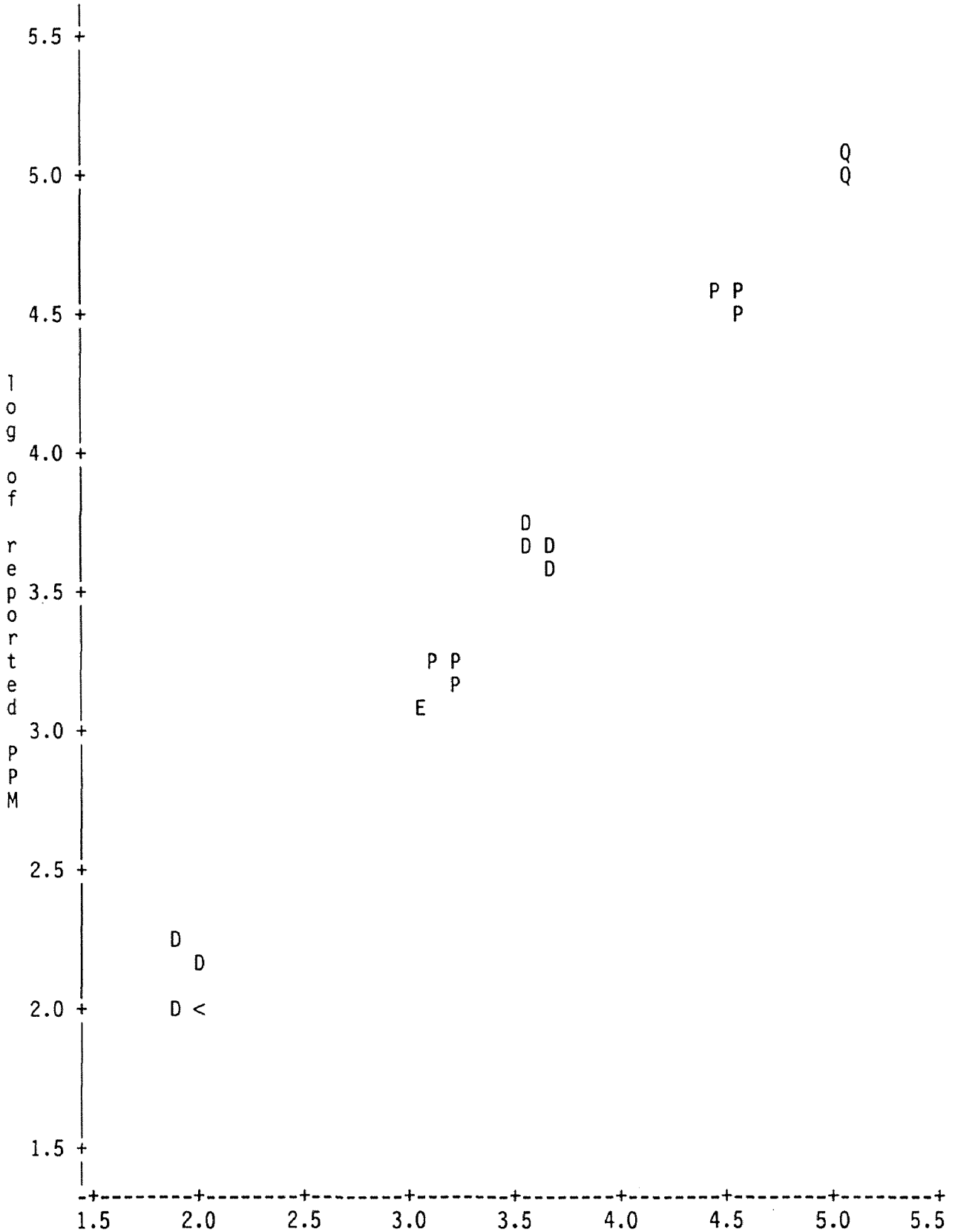
---------- METH=2 LAB=24 ----------

Plot of REC*LOGTRUE. Symbol is value of MTX.



---------- METH=2 LAB=24 ----------

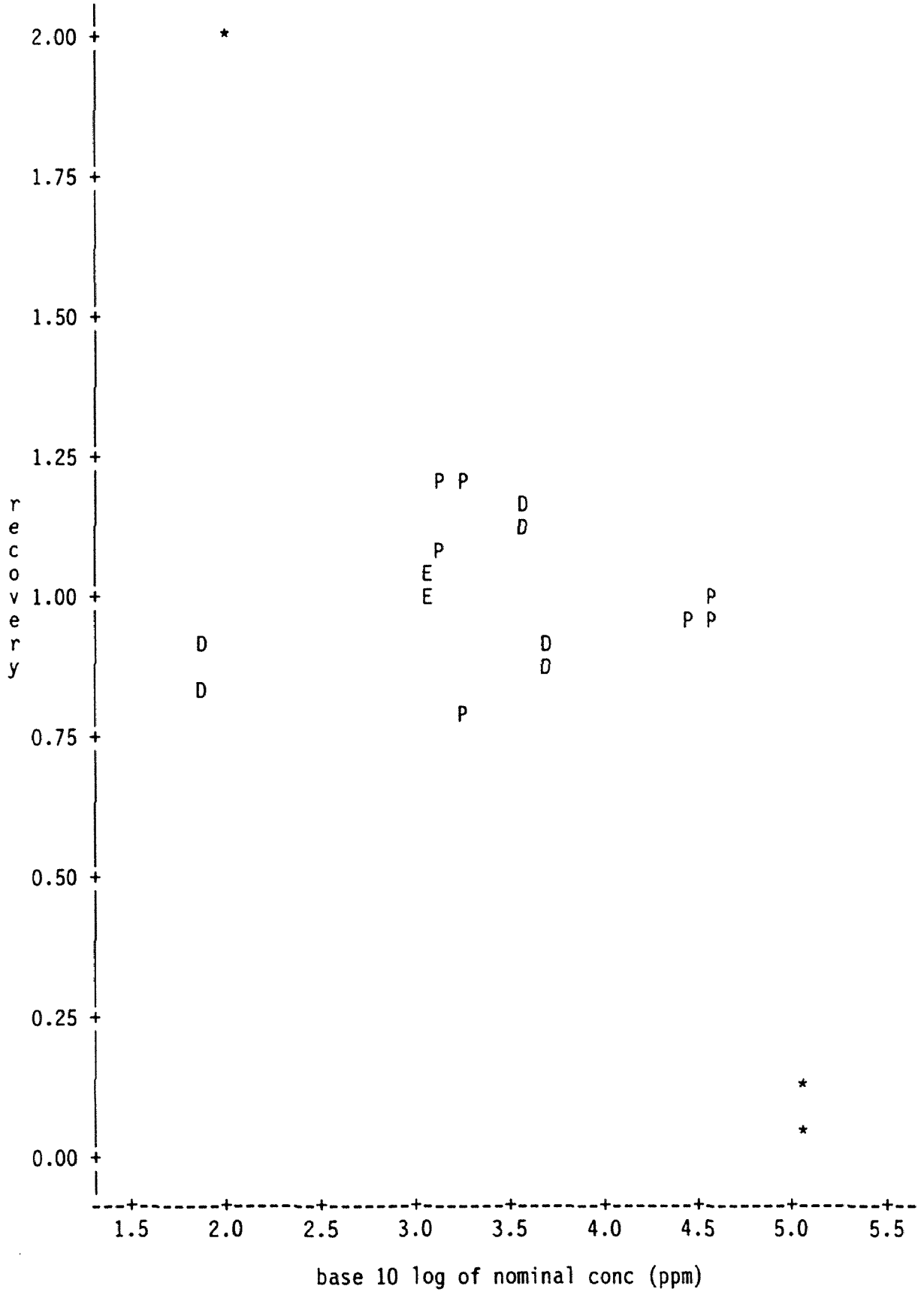
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 3 obs hidden.

---------- METH=2 LAB=25 ----------

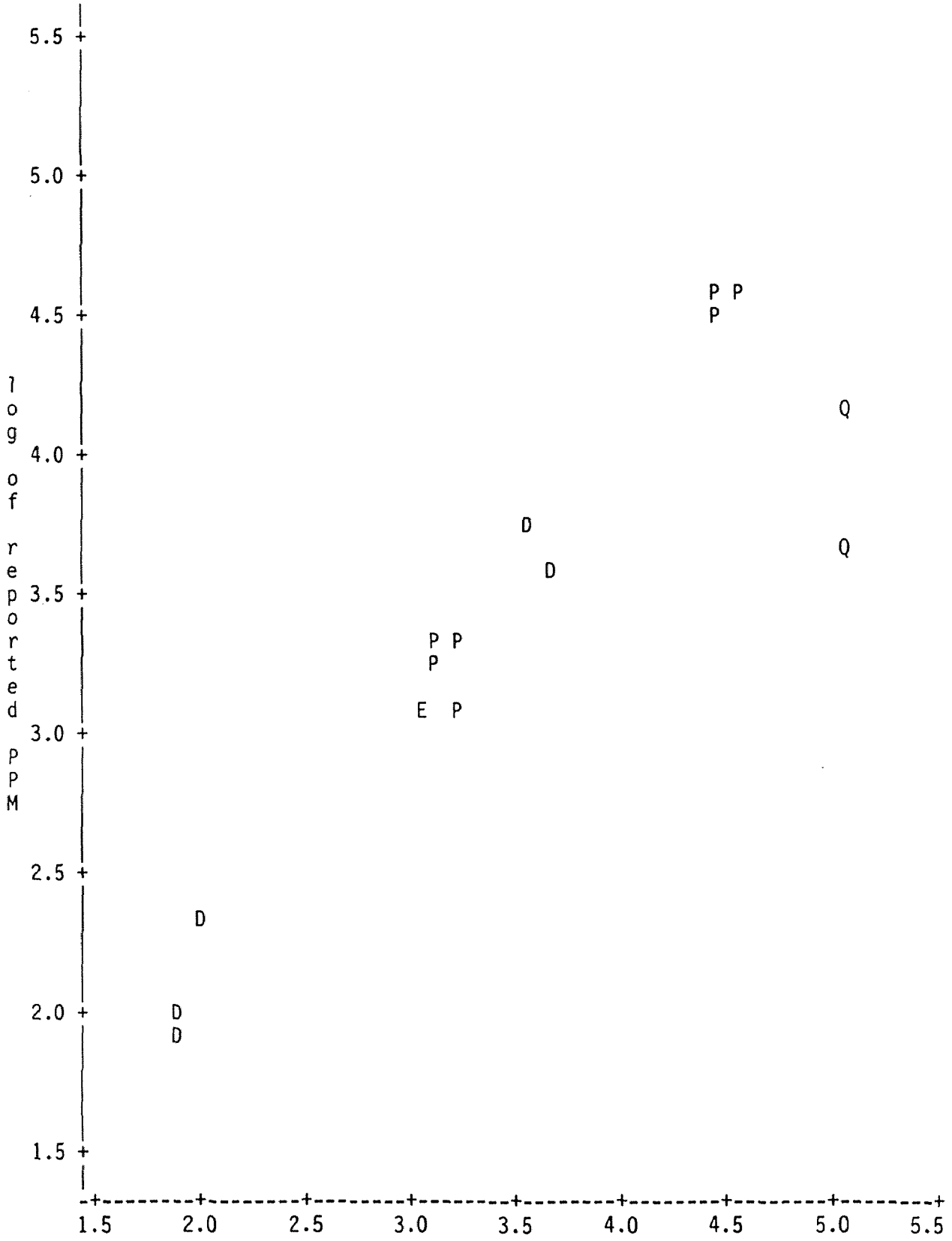
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 2 obs hidden.

---------- METH=2 LAB=25 ----------

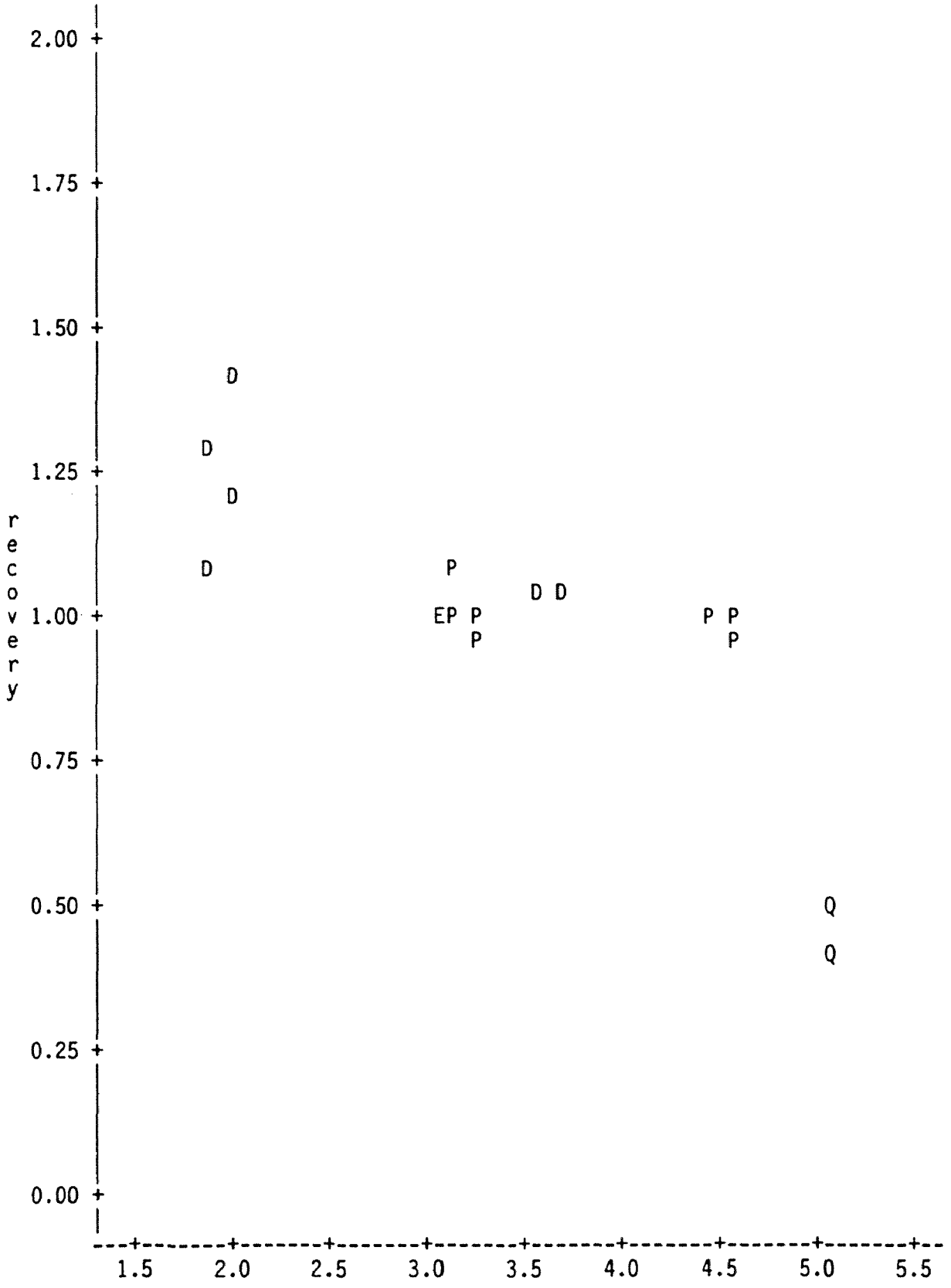
*Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.*



NOTE: 5 obs hidden.

---------- METH=2 LAB=26 ----------

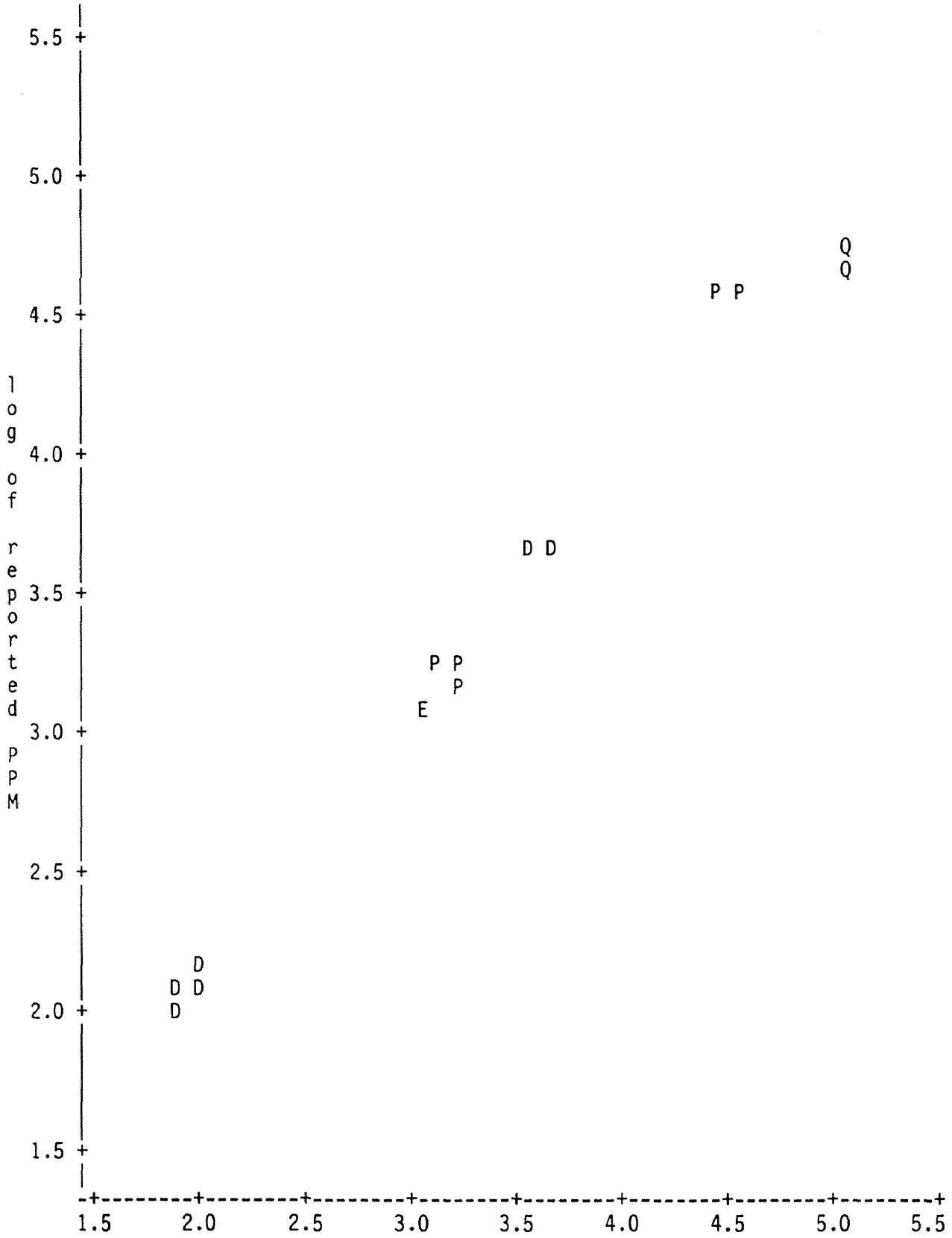
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 4 obs hidden.

---------- METH=2 LAB=26 ----------

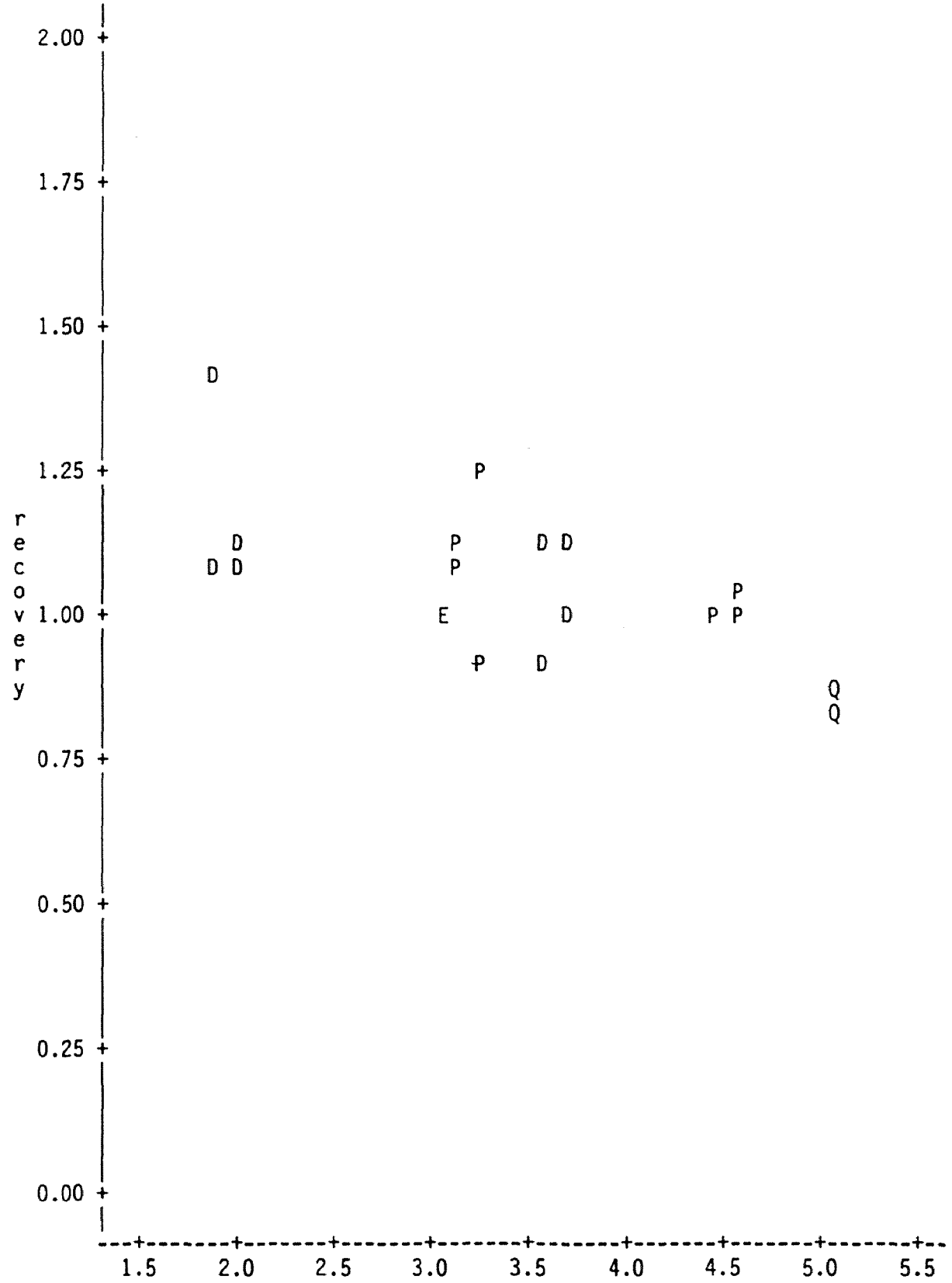
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 6 obs hidden.

---------- METH=2 LAB=27 ----------

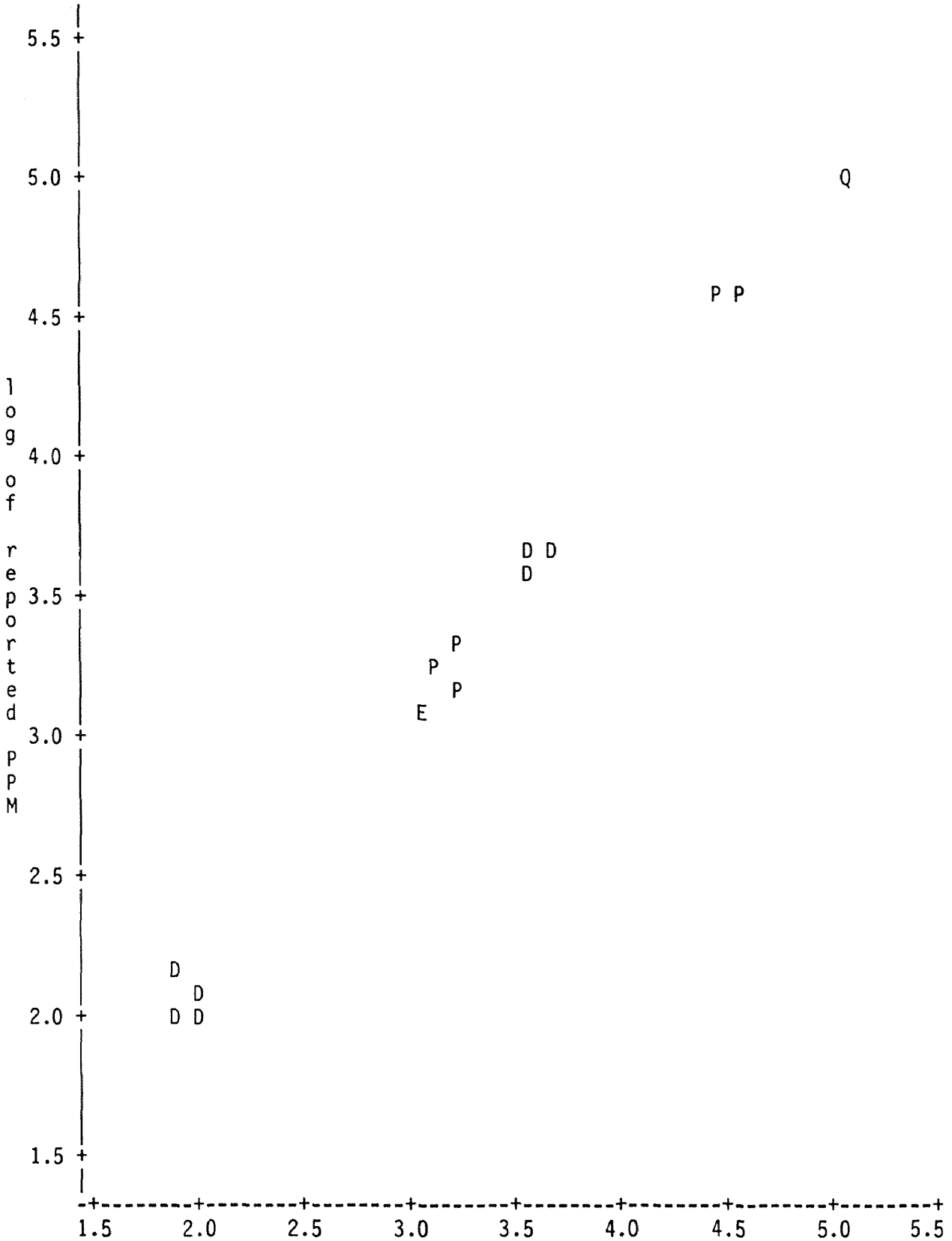
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 2 obs hidden.

---------- METH=2 LAB=27 ----------

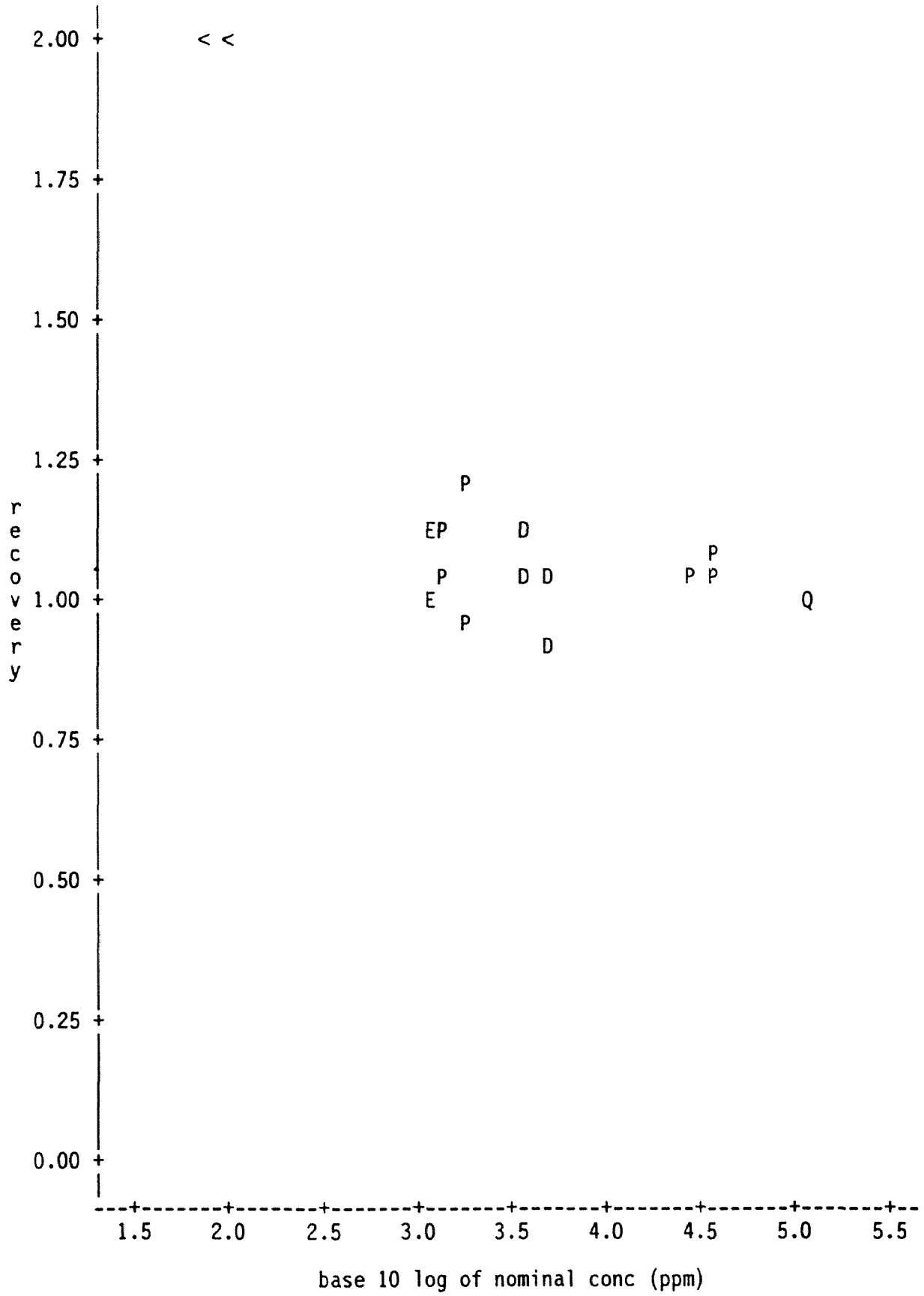
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 6 obs hidden.

---------- METH=2 LAB=28 ----------

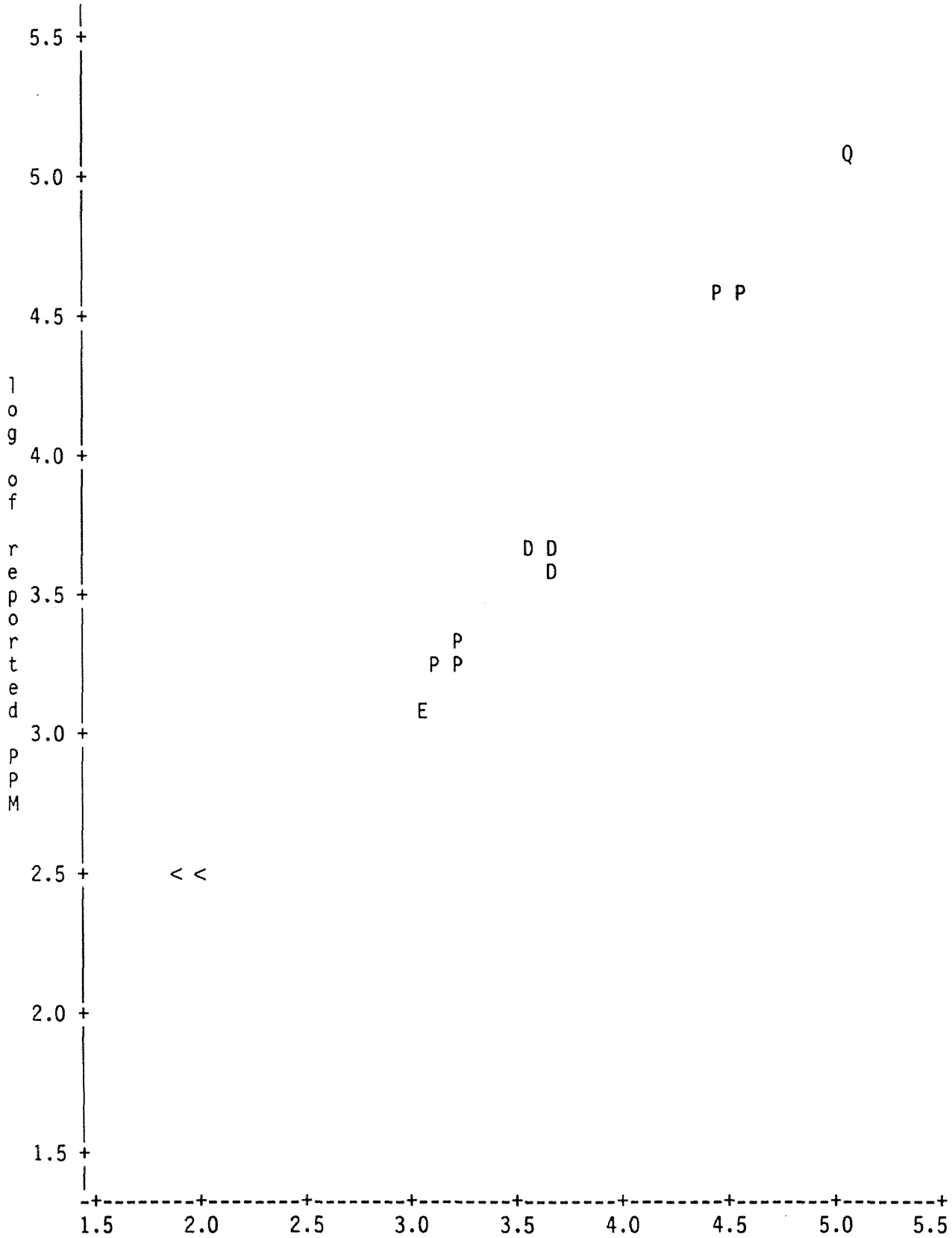
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 4 obs hidden.

---------- METH=2 LAB=28 ----------

Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



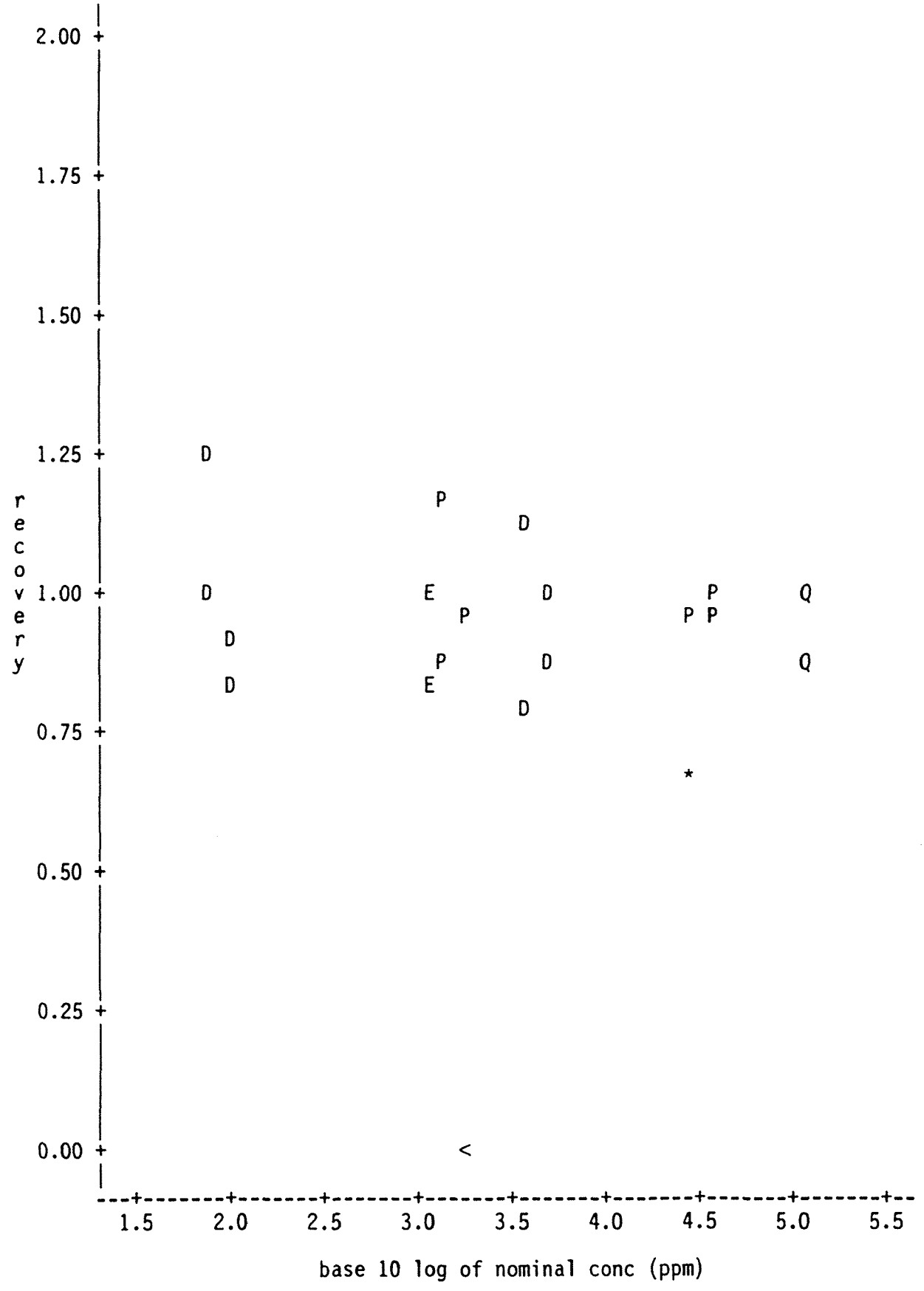
NOTE: 8 obs hidden.

Appendix G-7-3

MW/ICP Laboratories

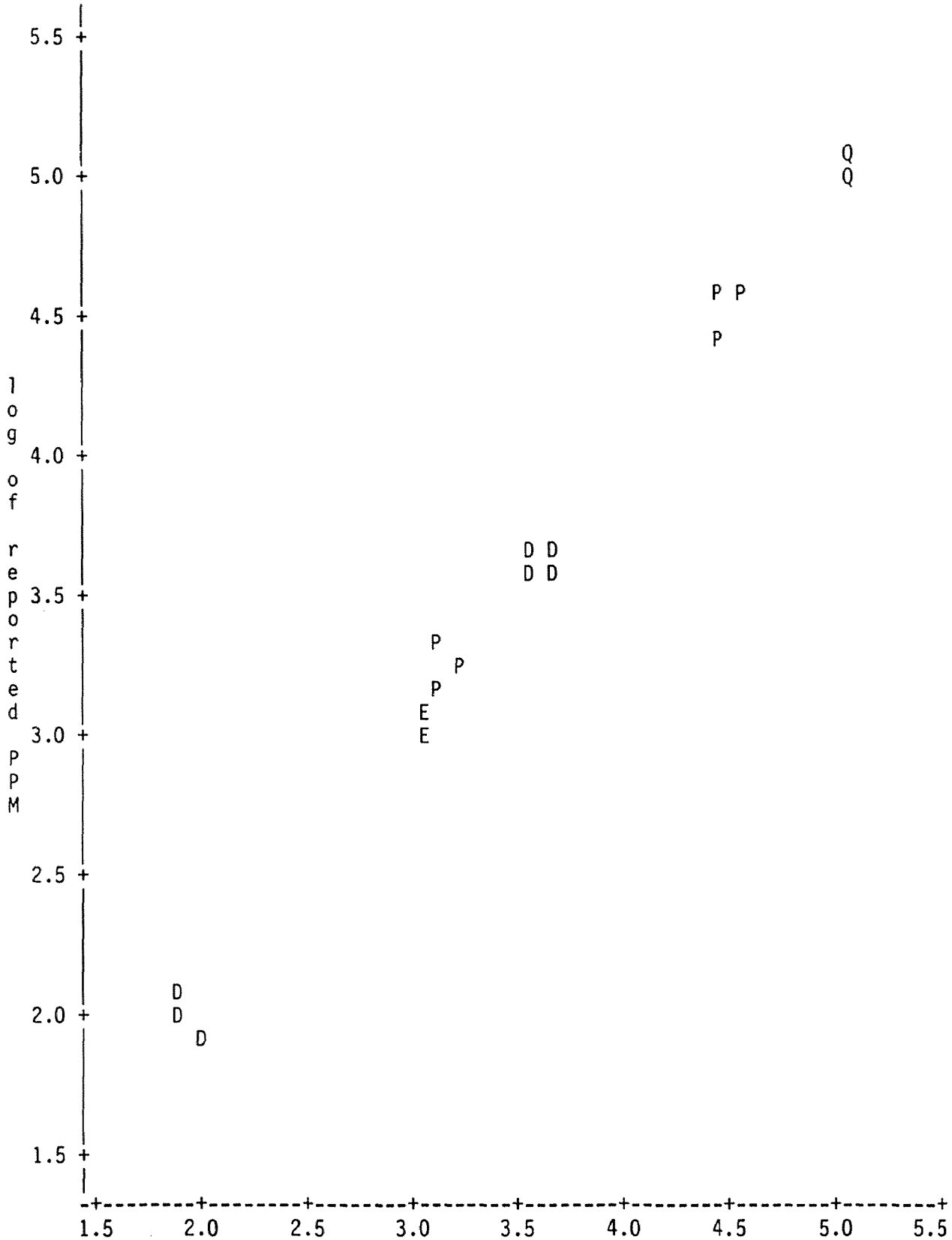
---------- METH=3 LAB=30 ----------

Plot of REC*LOGTRUE. Symbol is value of MTX.



---------- METH=3 LAB=30 ----------

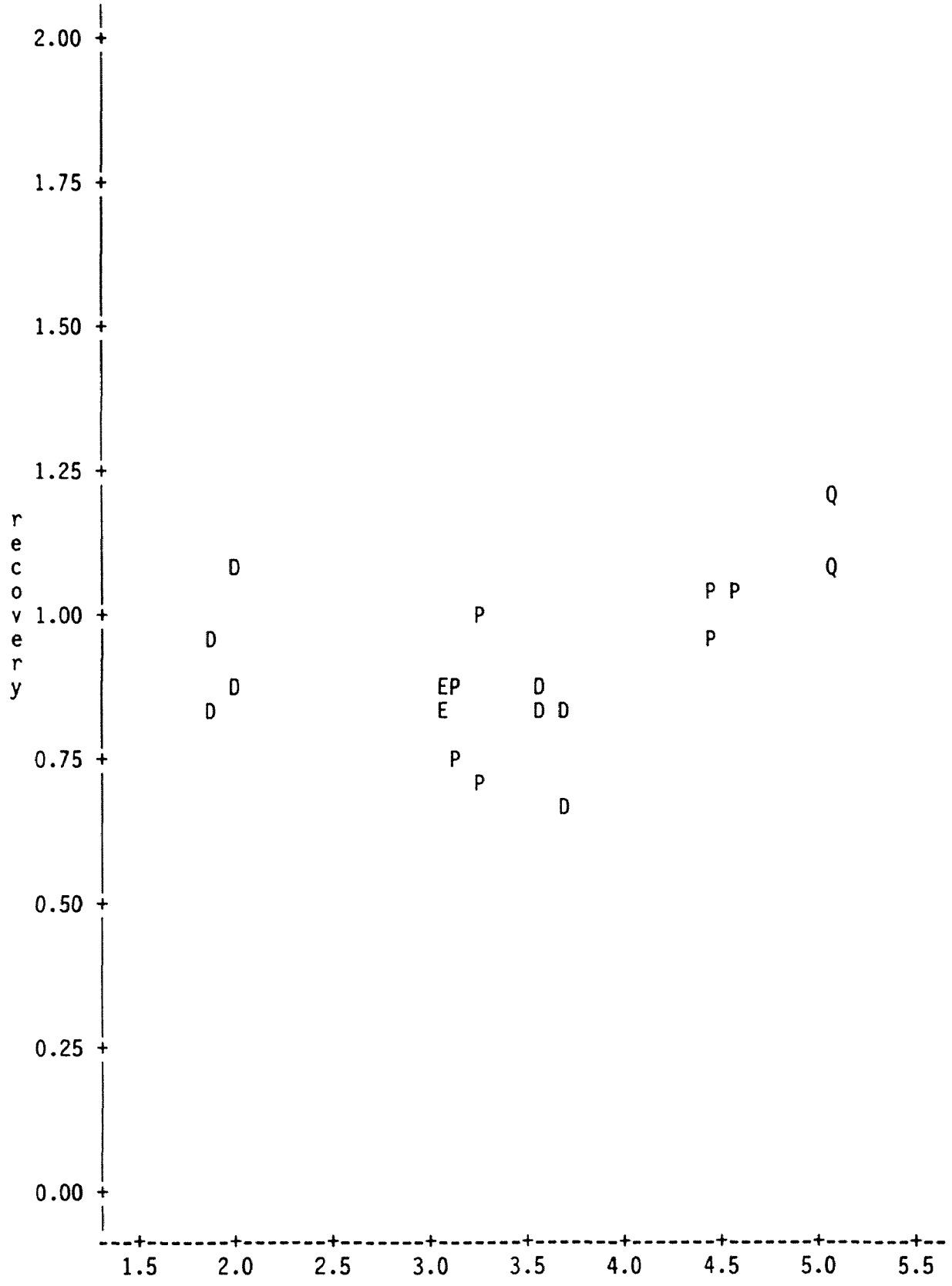
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 2 obs hidden. 1 obs were out of range.

---------- METH=3 LAB=31 ----------

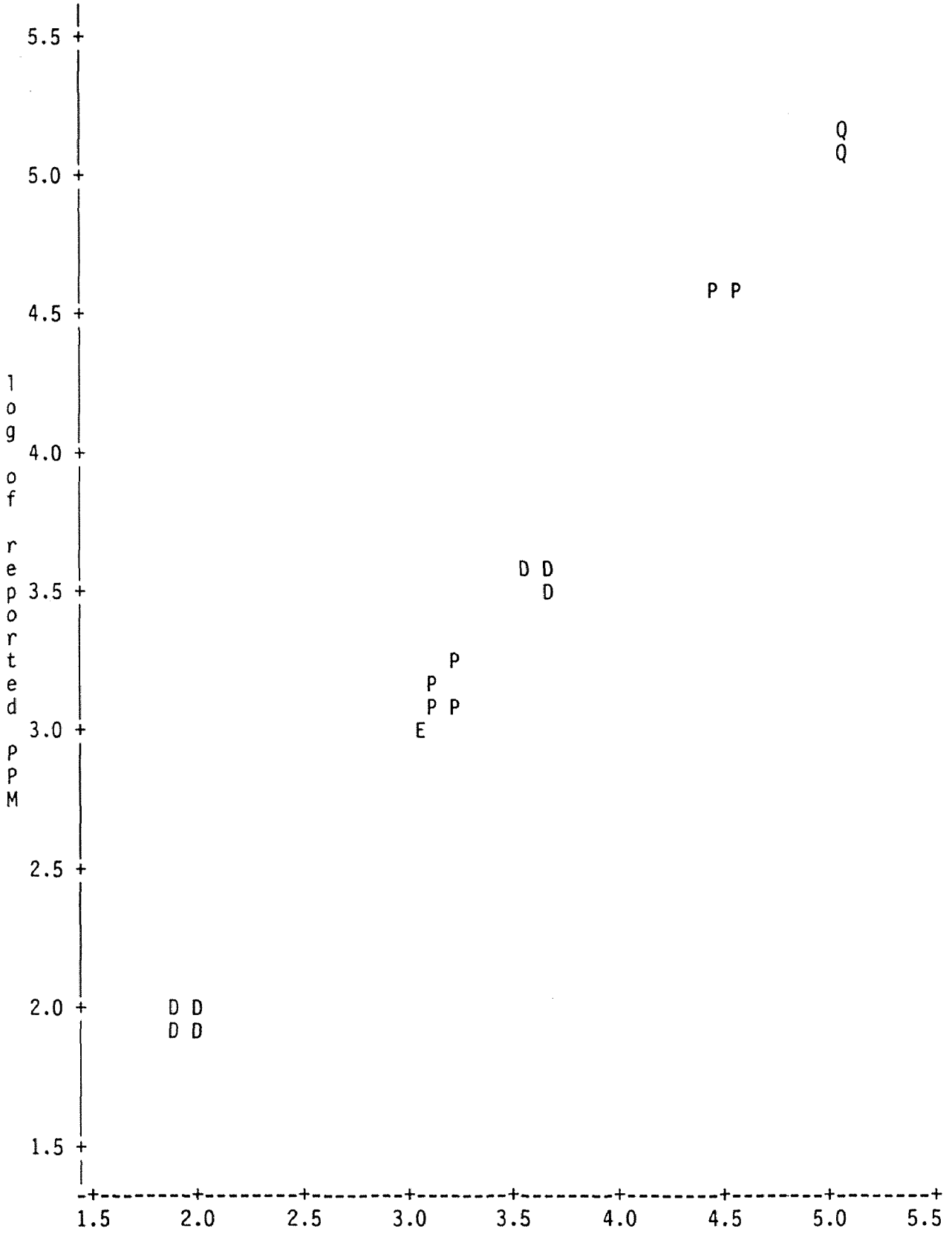
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 1 obs hidden.

---------- METH=3 LAB=31 ----------

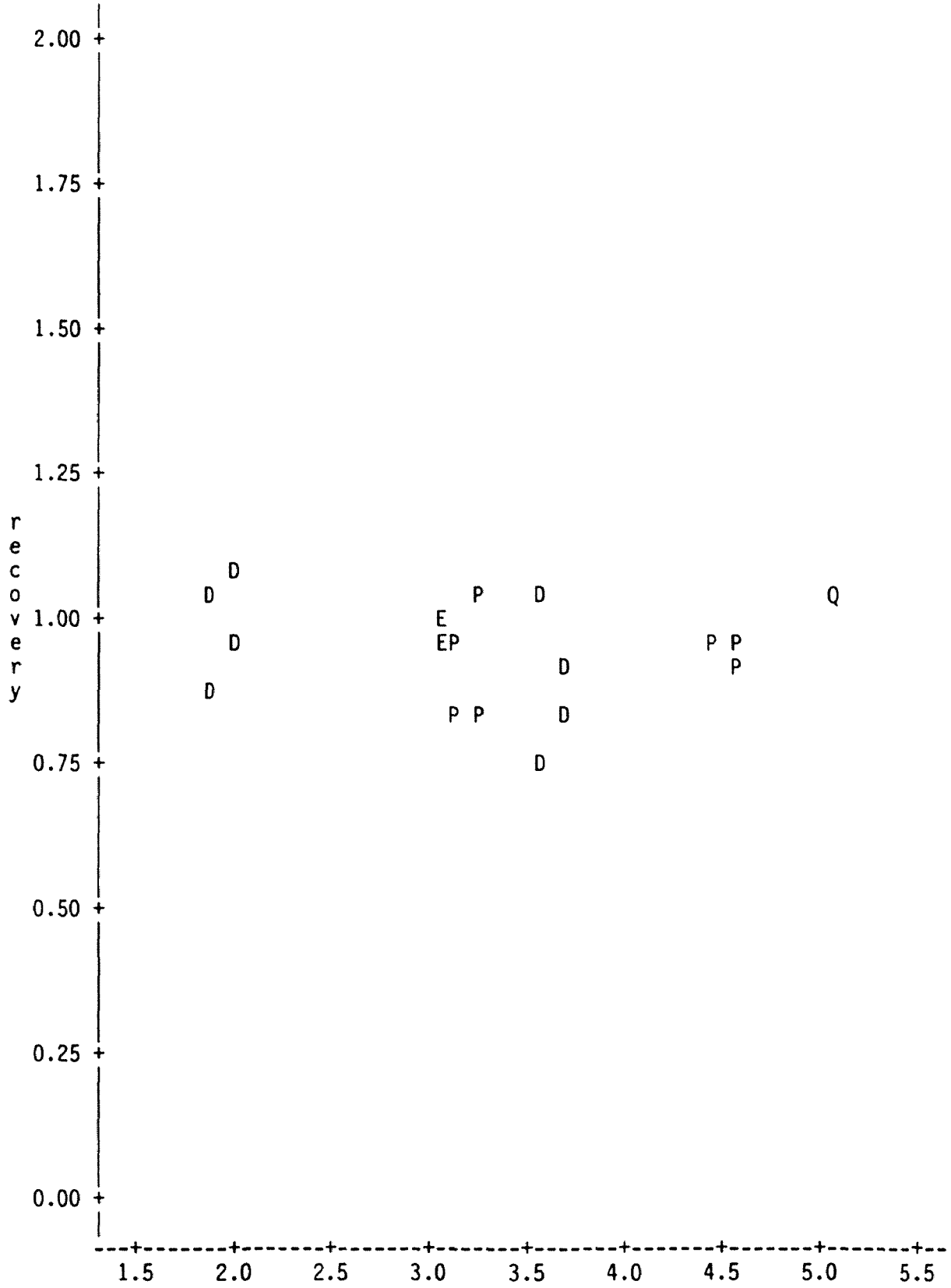
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 4 obs hidden.

---------- METH=3 LAB=32 ----------

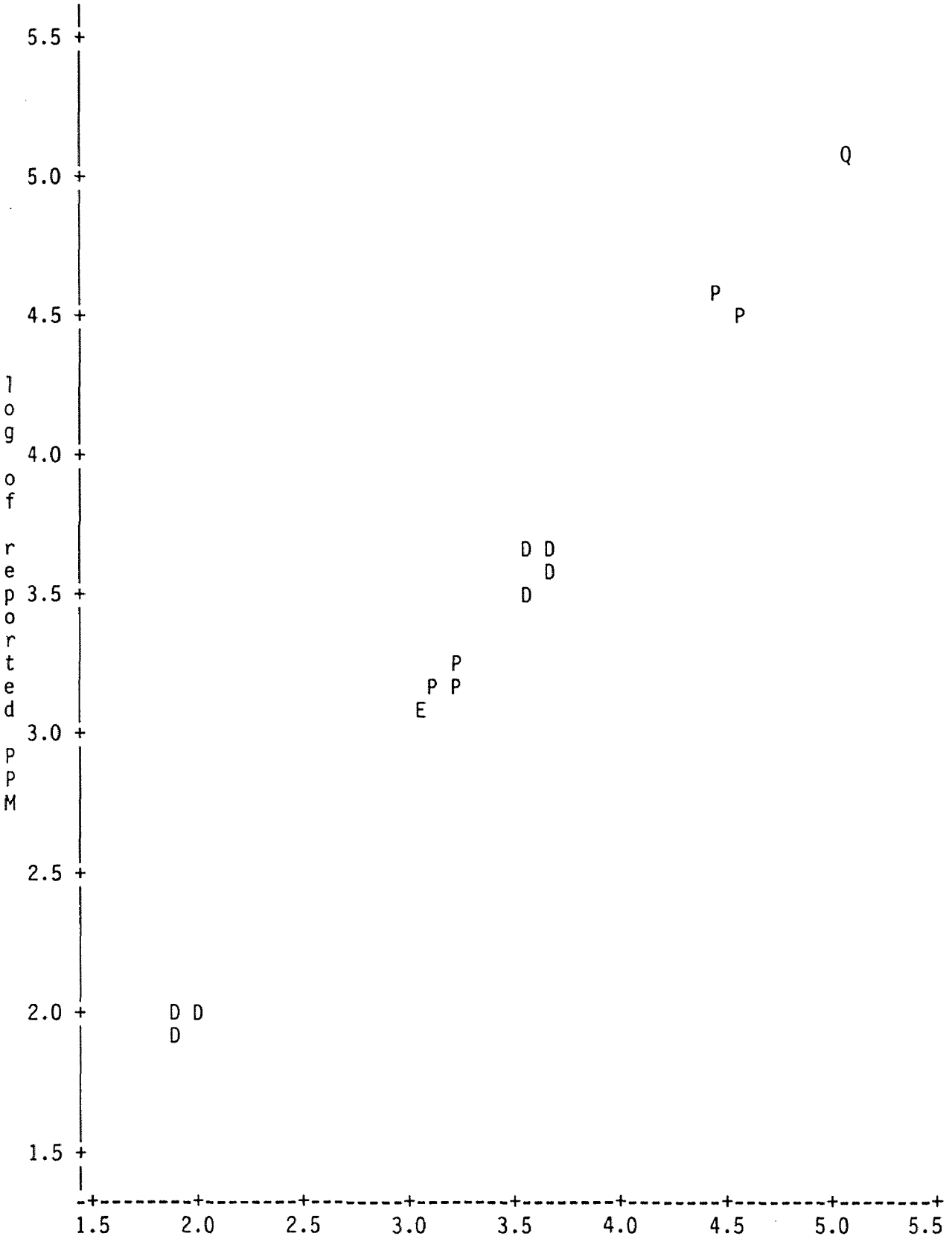
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 2 obs hidden.

---------- METH=3 LAB=32 ----------

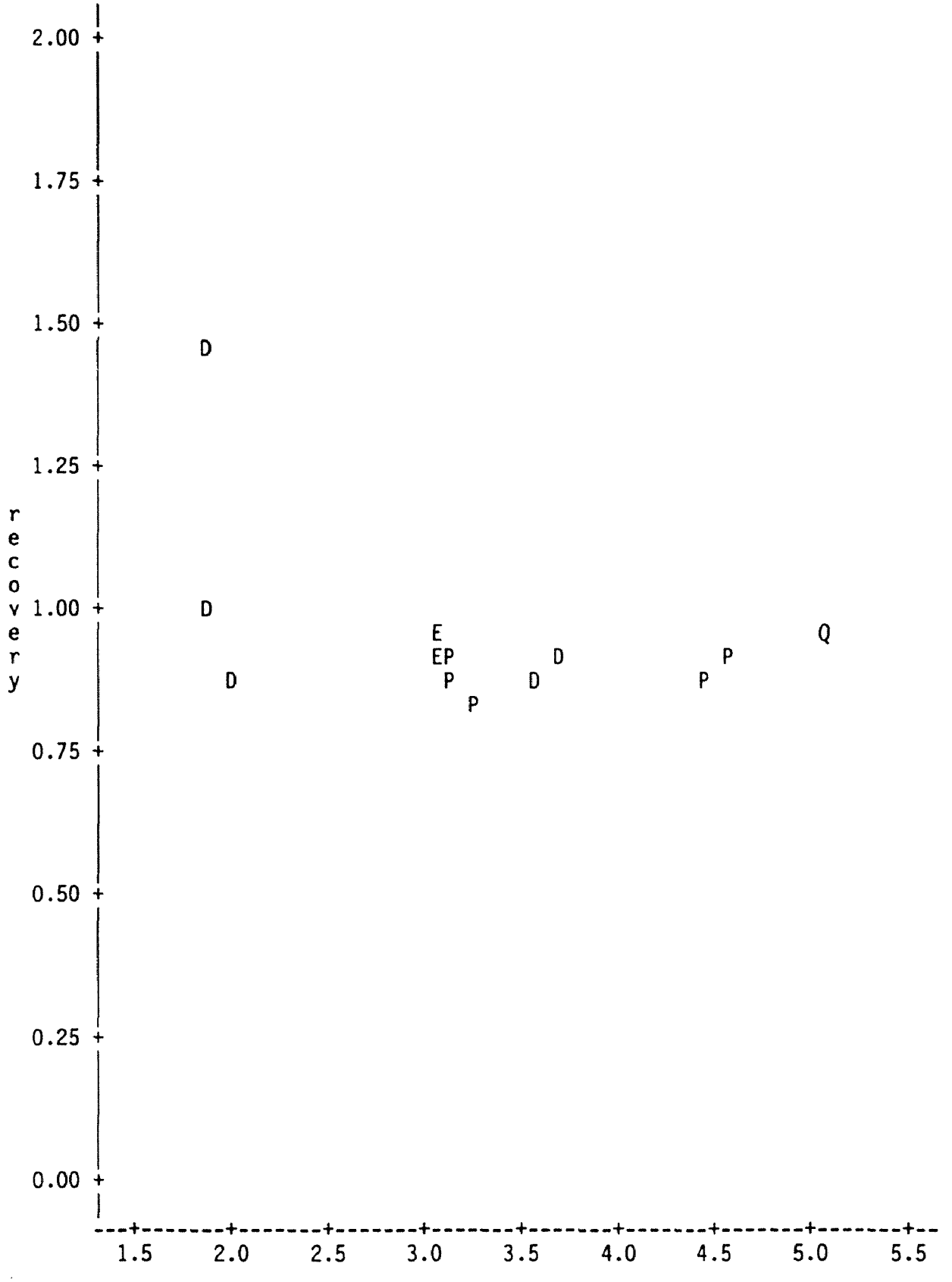
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 6 obs hidden.

---------- METH=3 LAB=33 ----------

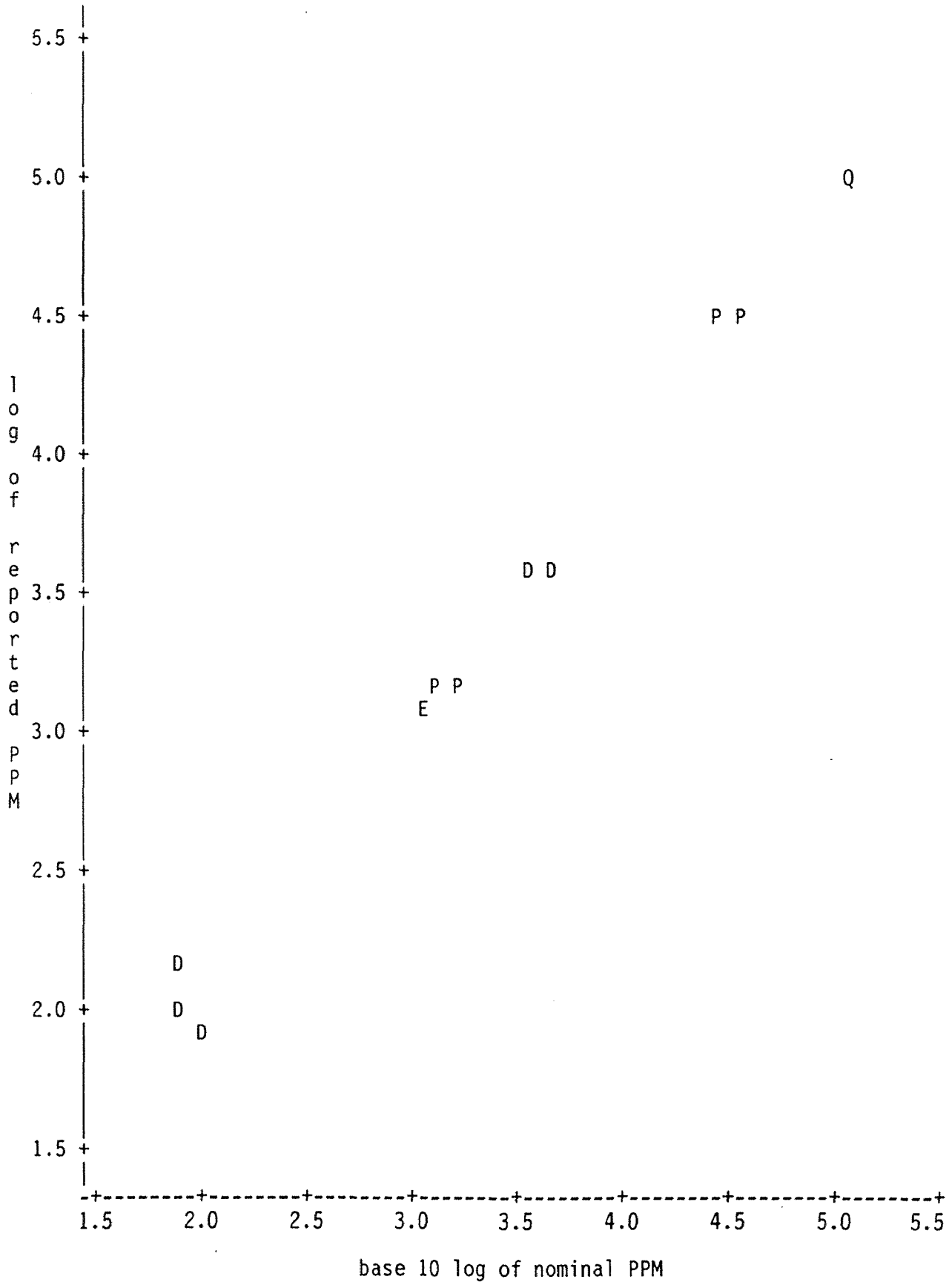
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 7 obs hidden.

---------- METH=3 LAB=33 ----------

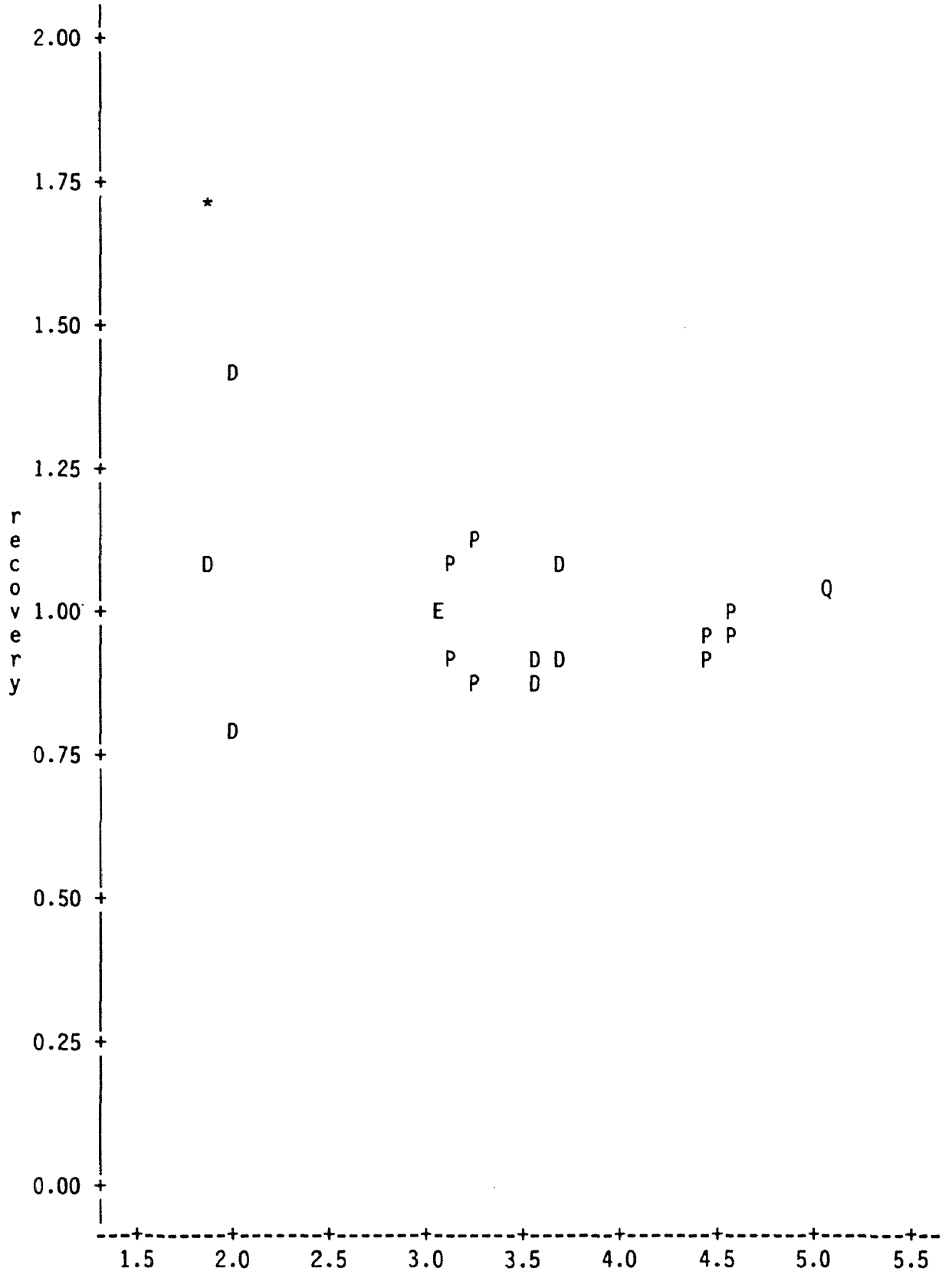
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 9 obs hidden.

---------- METH=3 LAB=34 ----------

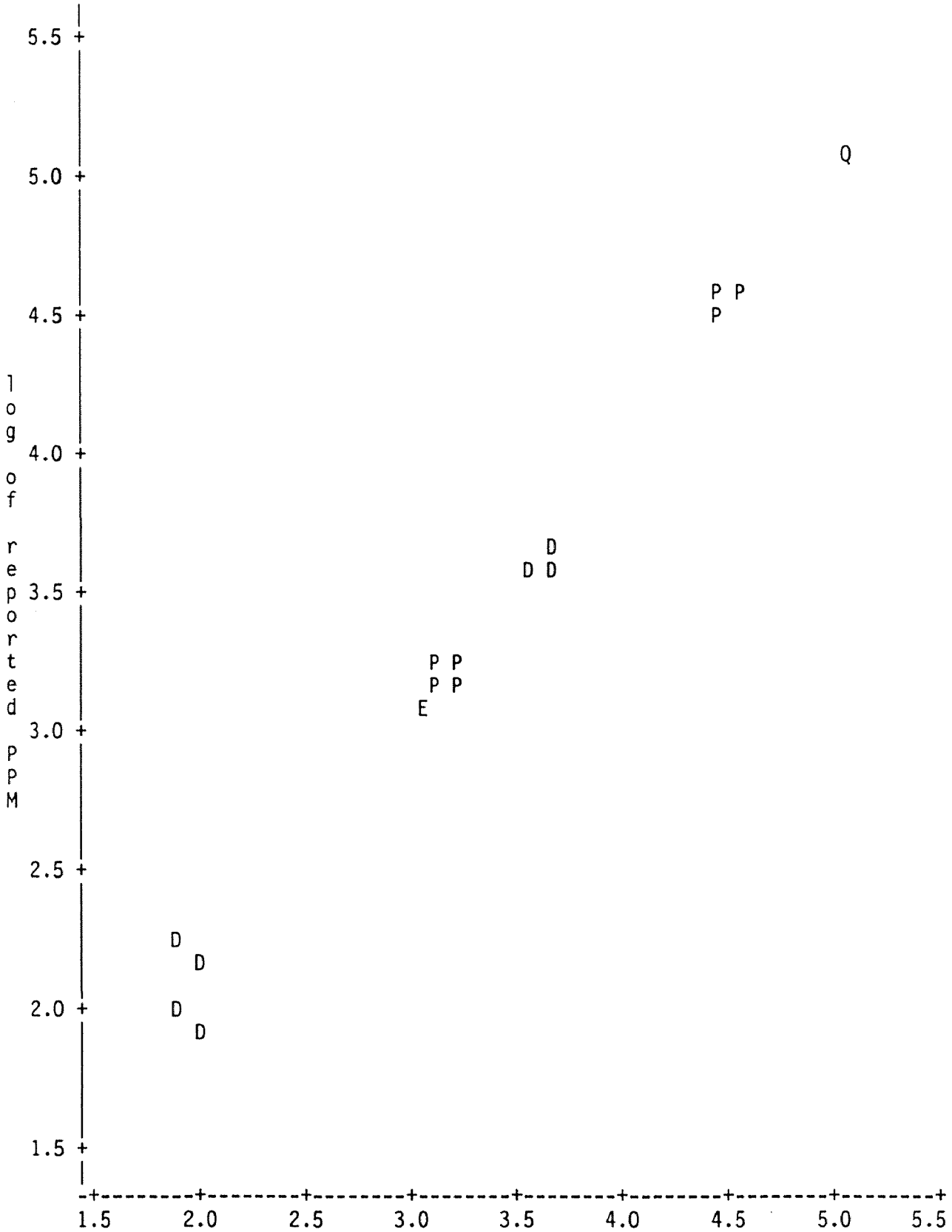
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 2 obs hidden.

---------- METH=3 LAB=34 ----------

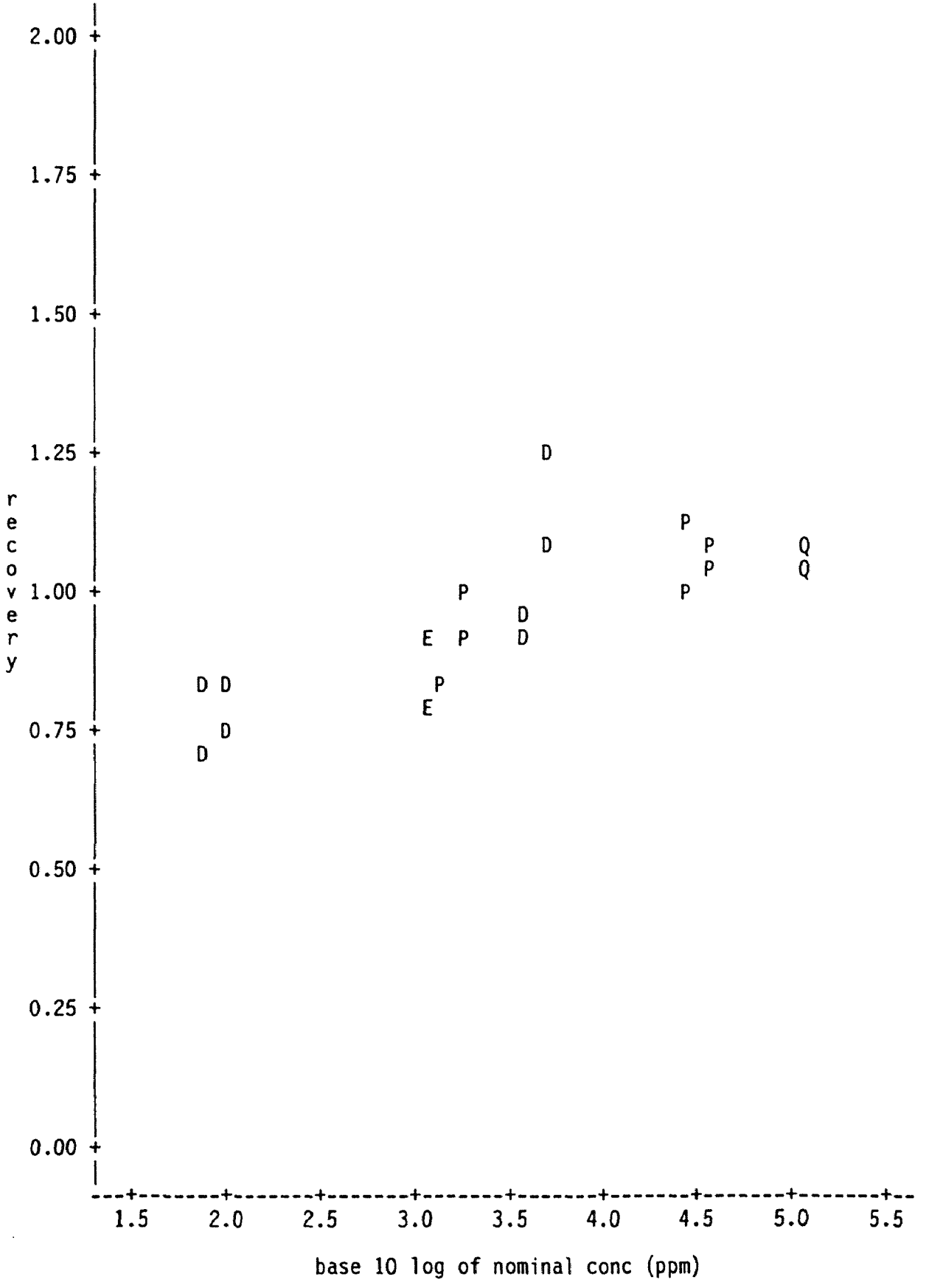
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 4 obs hidden.

---------- METH=3 LAB=35 ----------

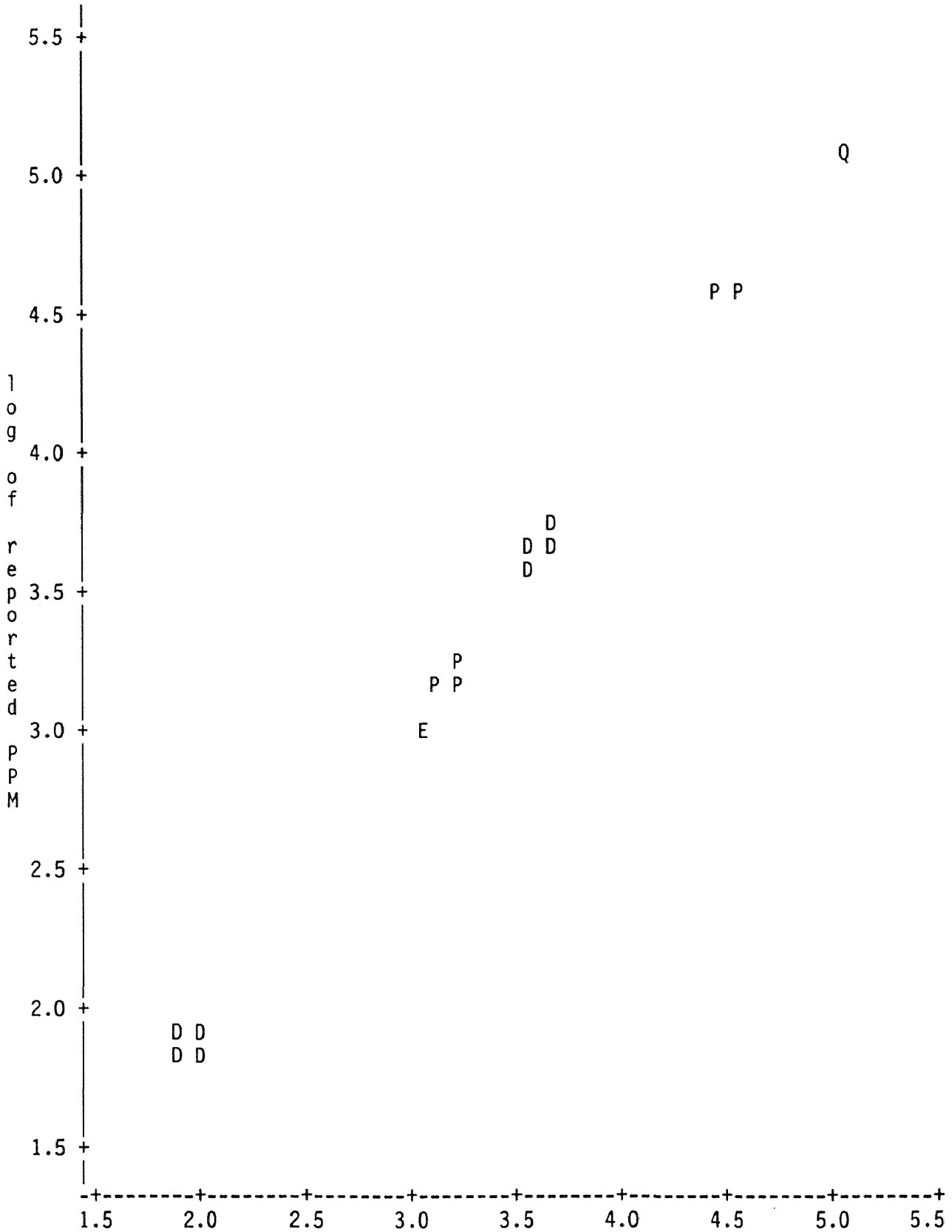
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 1 obs hidden.

---------- METH=3 LAB=35 ----------

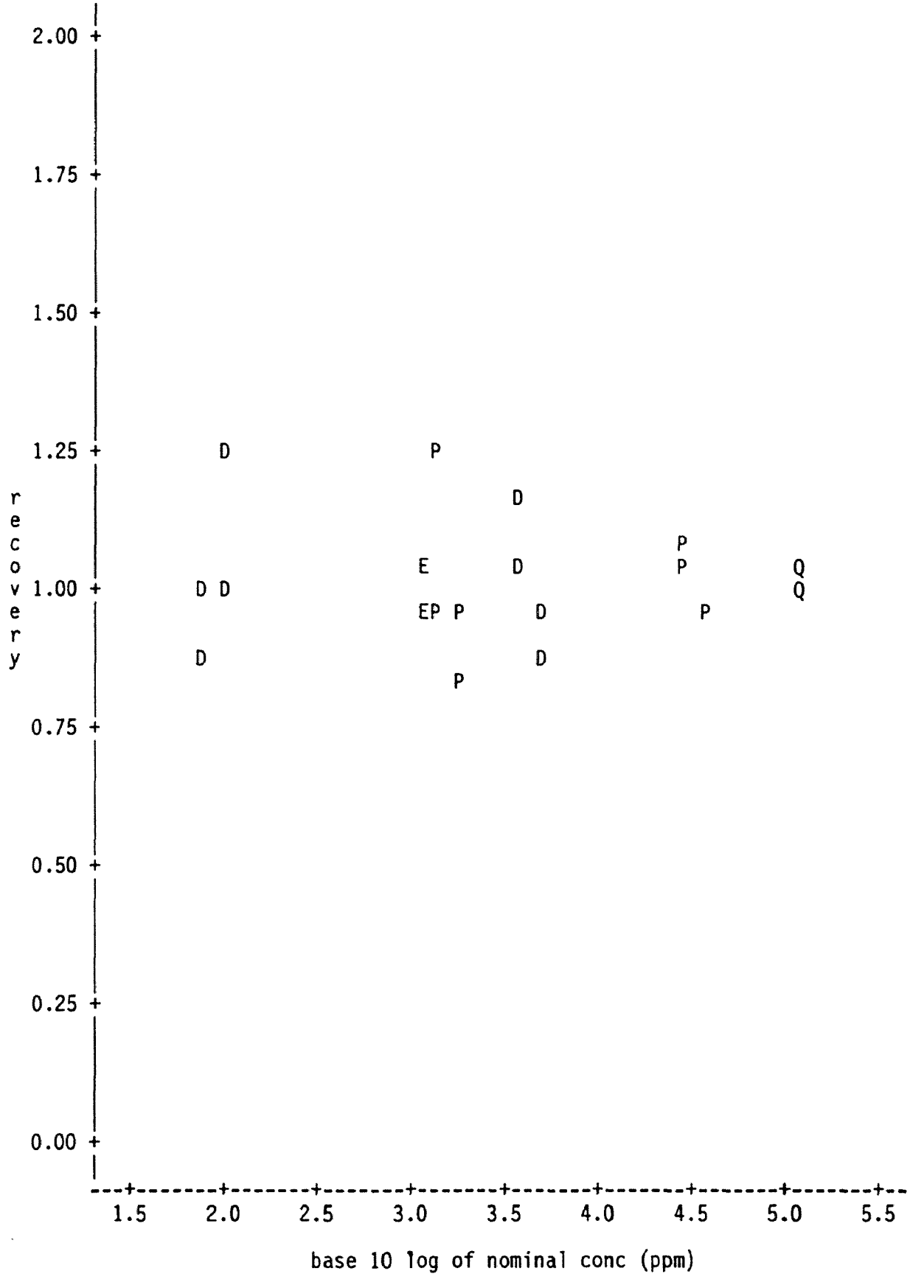
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 5 obs hidden.

---------- METH=3 LAB=36 ----------

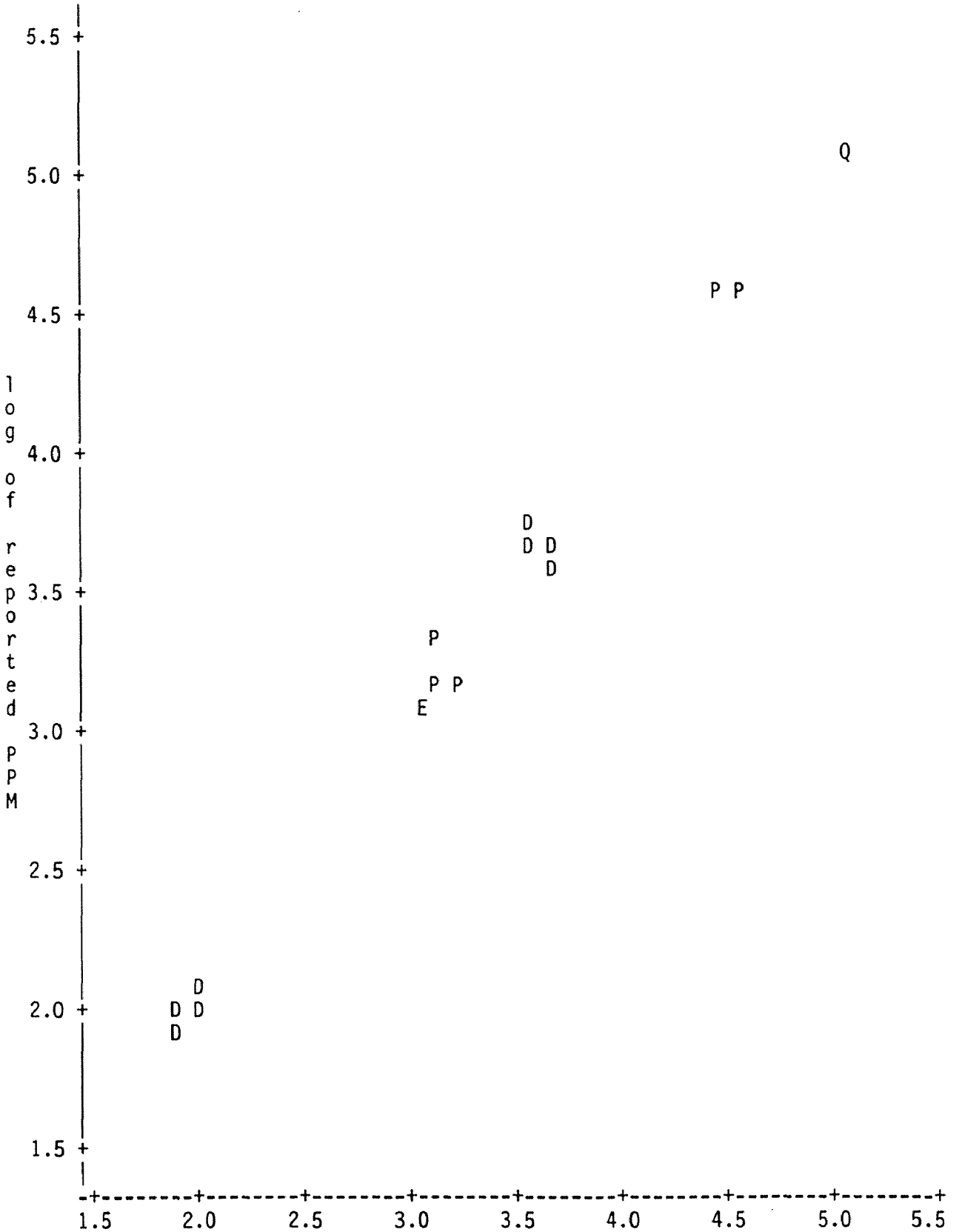
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 1 obs hidden.

---------- METH=3 LAB=36 ----------

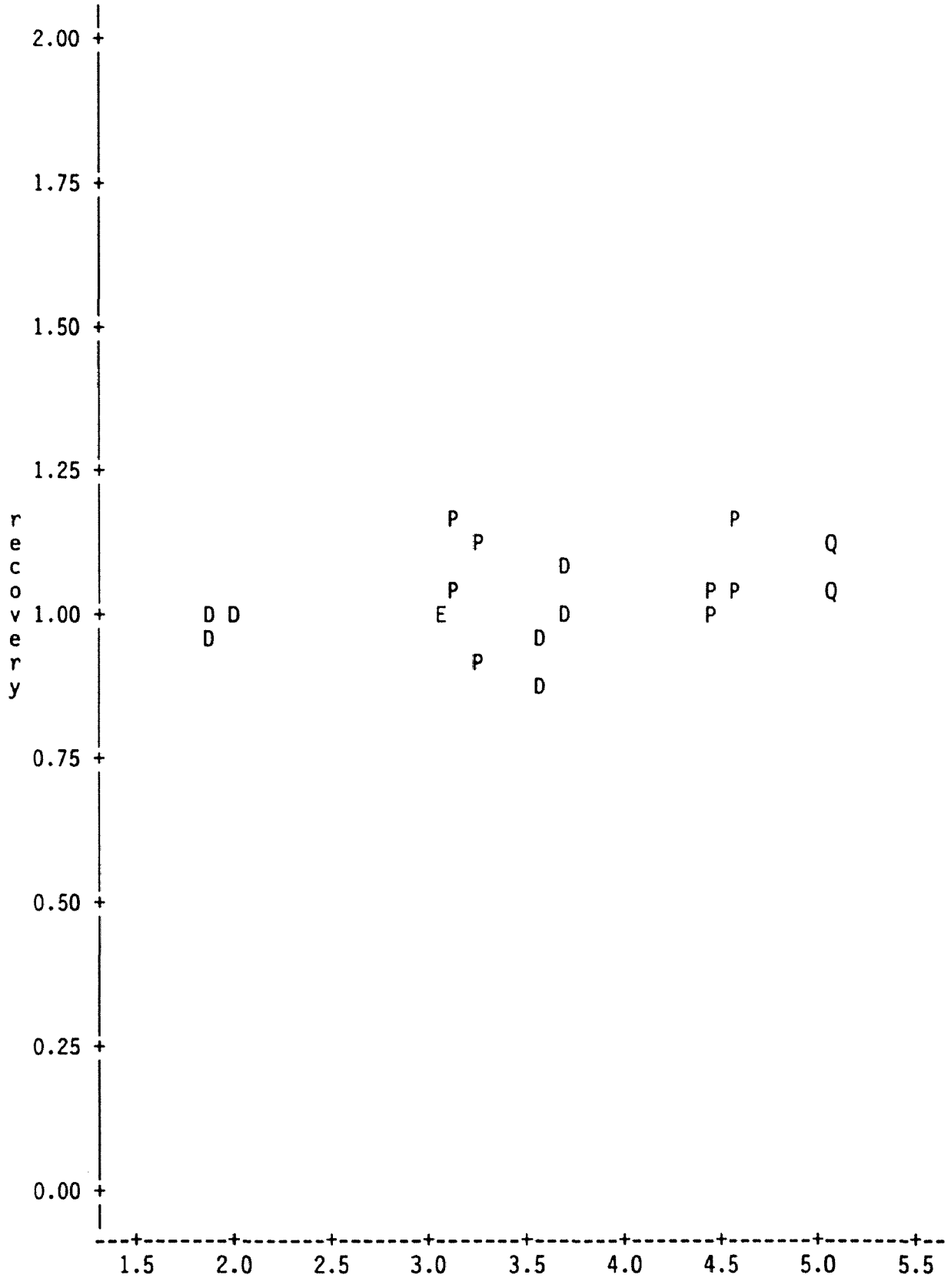
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 5 obs hidden.

---------- METH=3 LAB=37 ----------

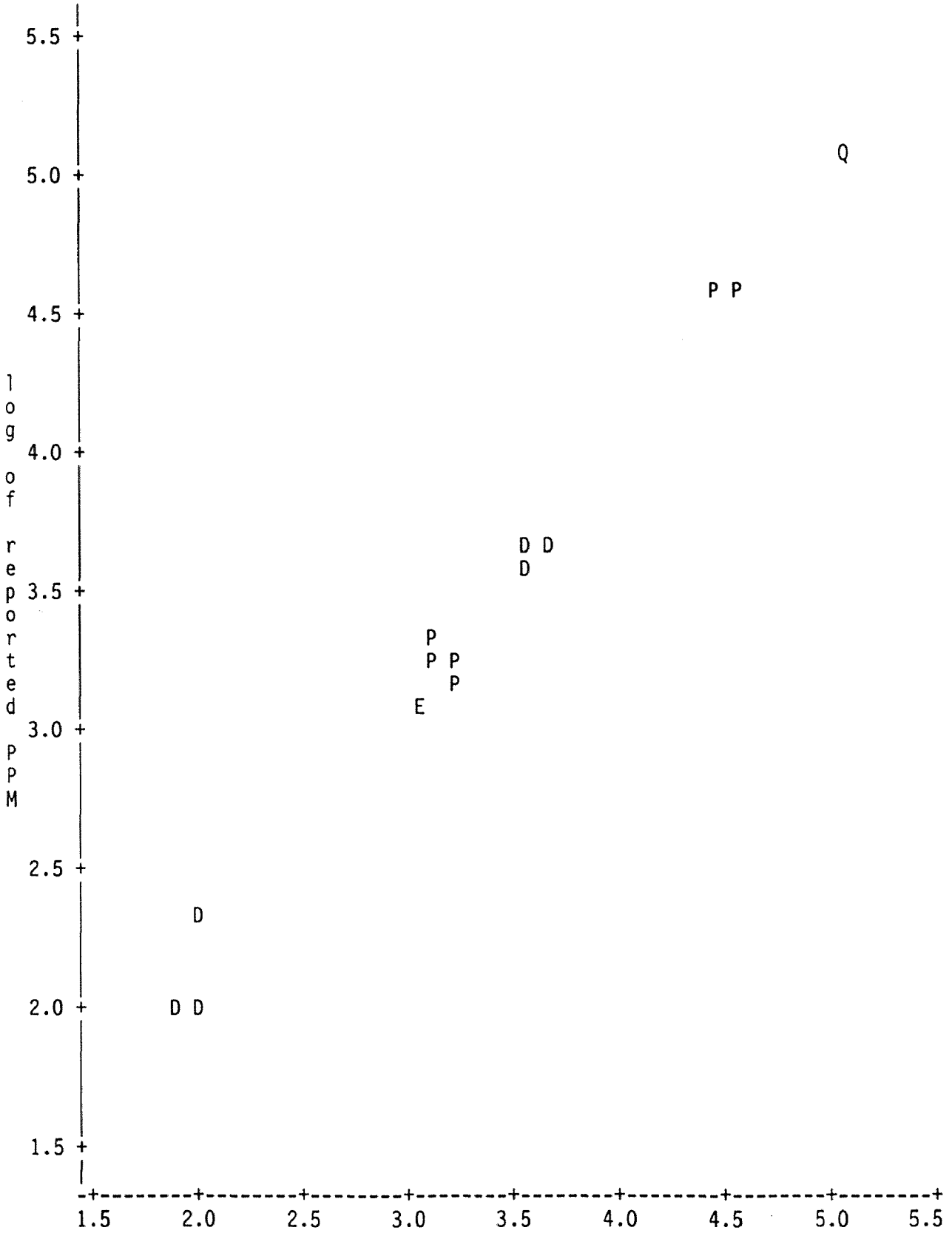
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 1 obs hidden.

---------- METH=3 LAB=37 ----------

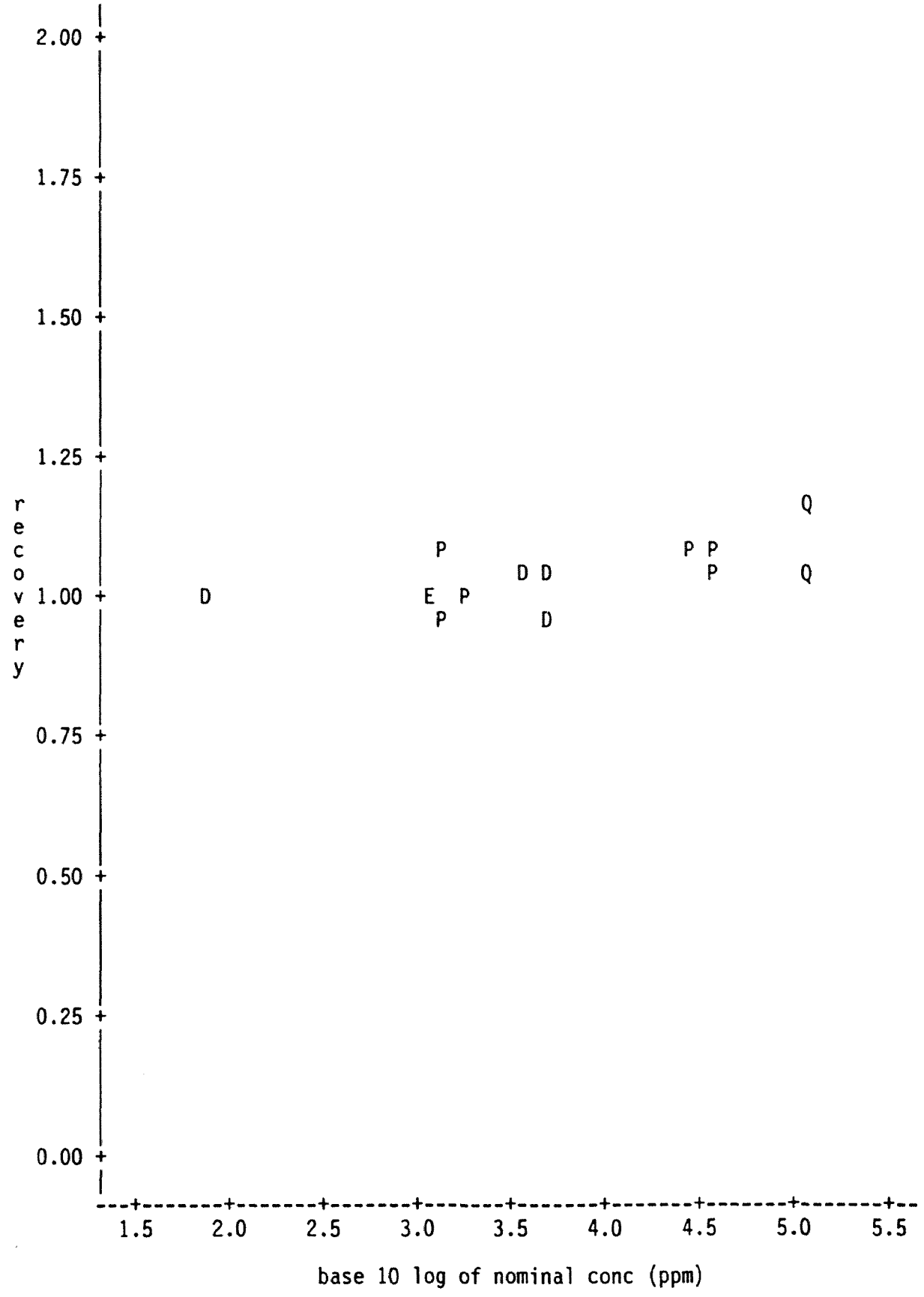
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 6 obs hidden.

---------- METH=3 LAB=38 ----------

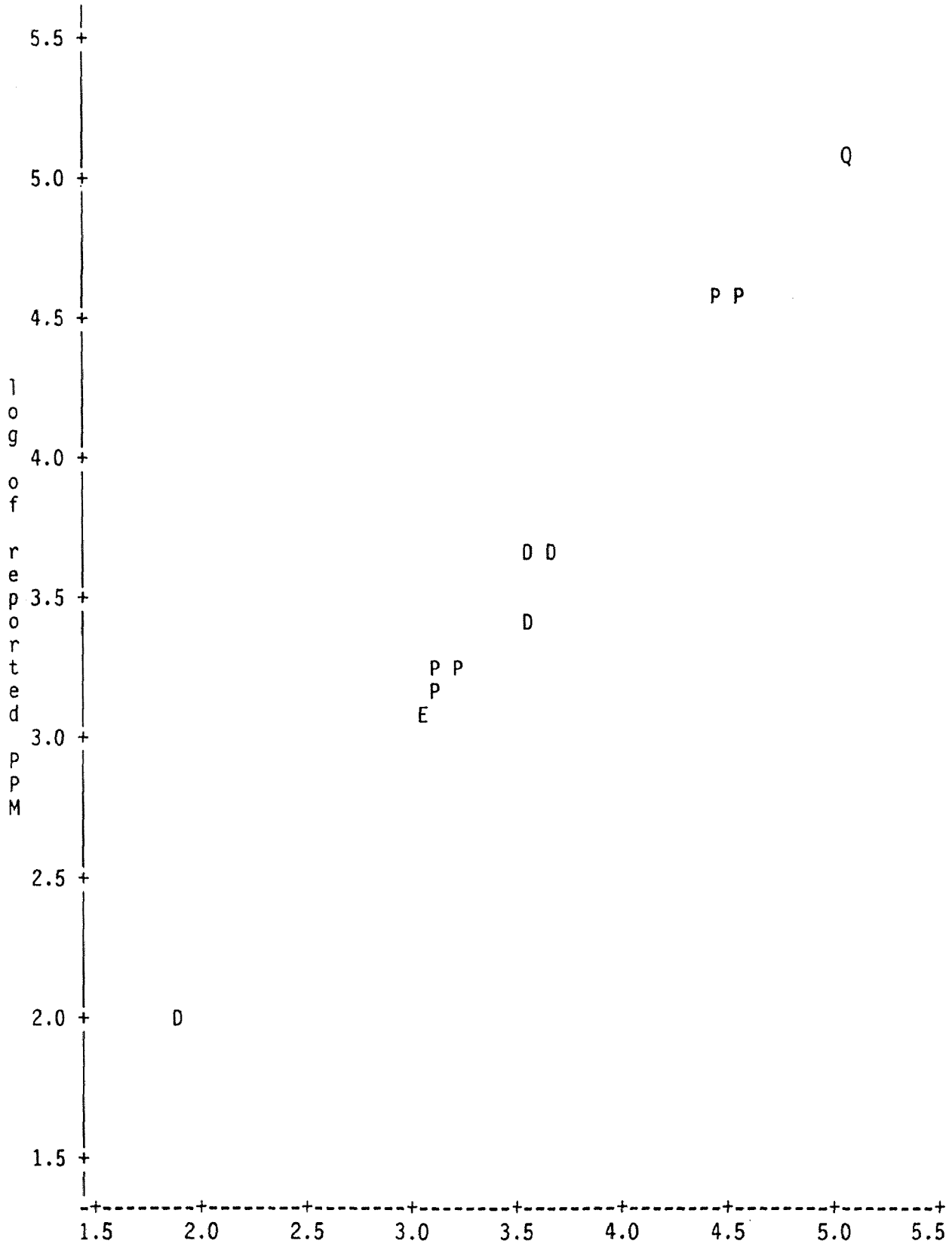
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 3 obs hidden.

---------- METH=3 LAB=38 ----------

Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



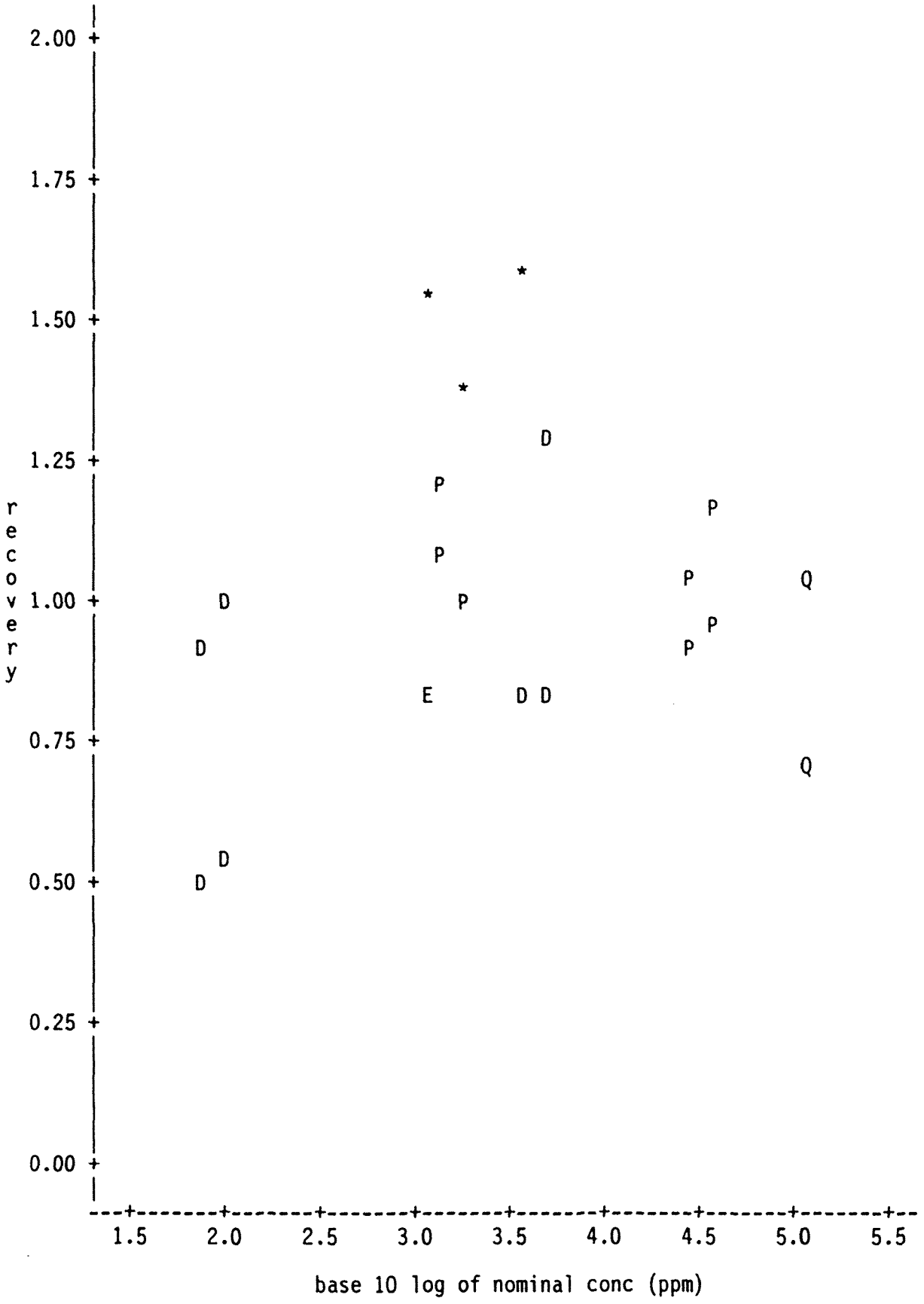
NOTE: 5 obs hidden. 3 obs were out of range.

Appendix G-7-4

HP/ICP Laboratories

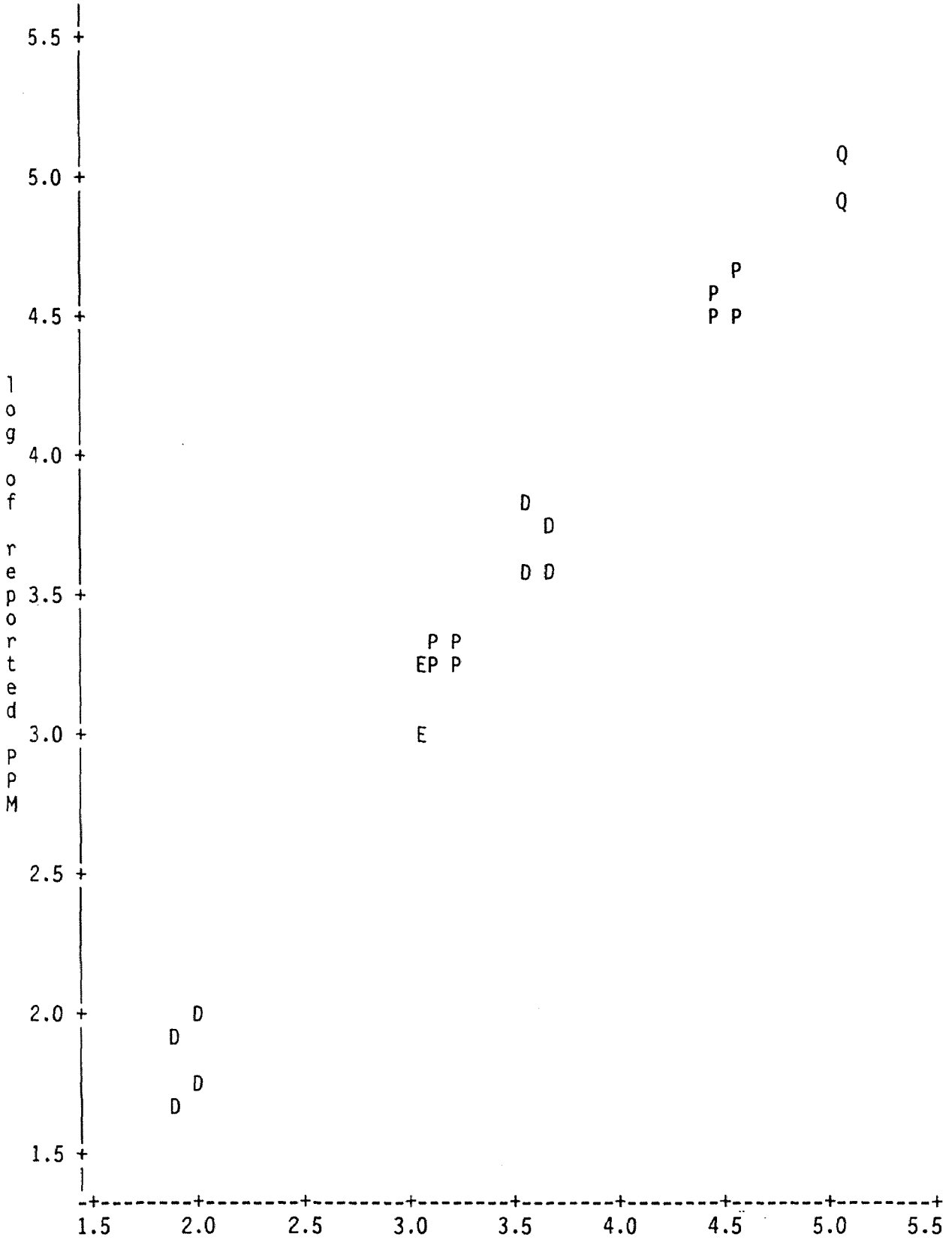
---------- METH=4 LAB=40 ----------

Plot of REC*LOGTRUE. Symbol is value of MTX.



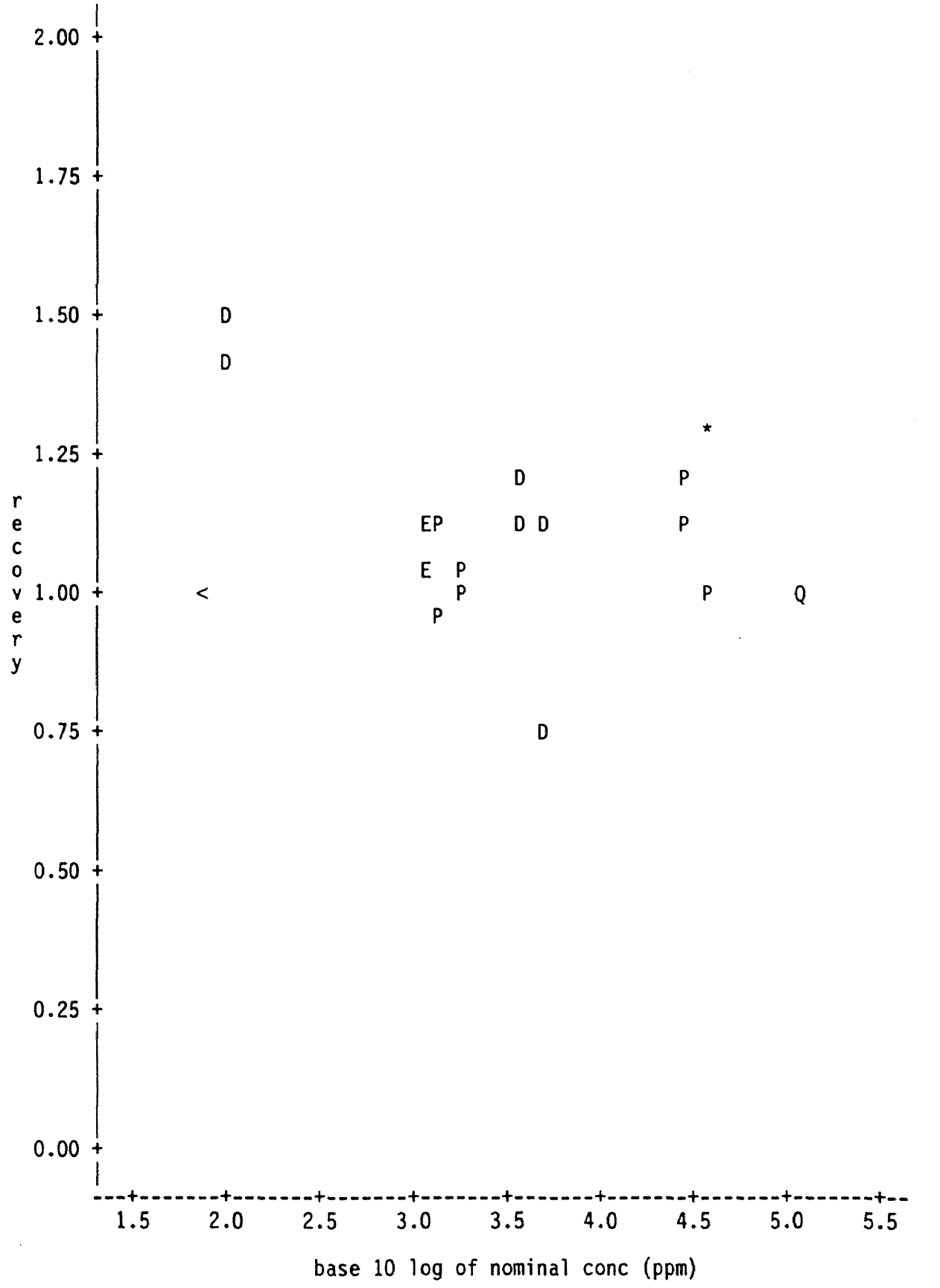
---------- METH=4 LAB=40 ----------

Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



---------- METH=4 LAB=41 ----------

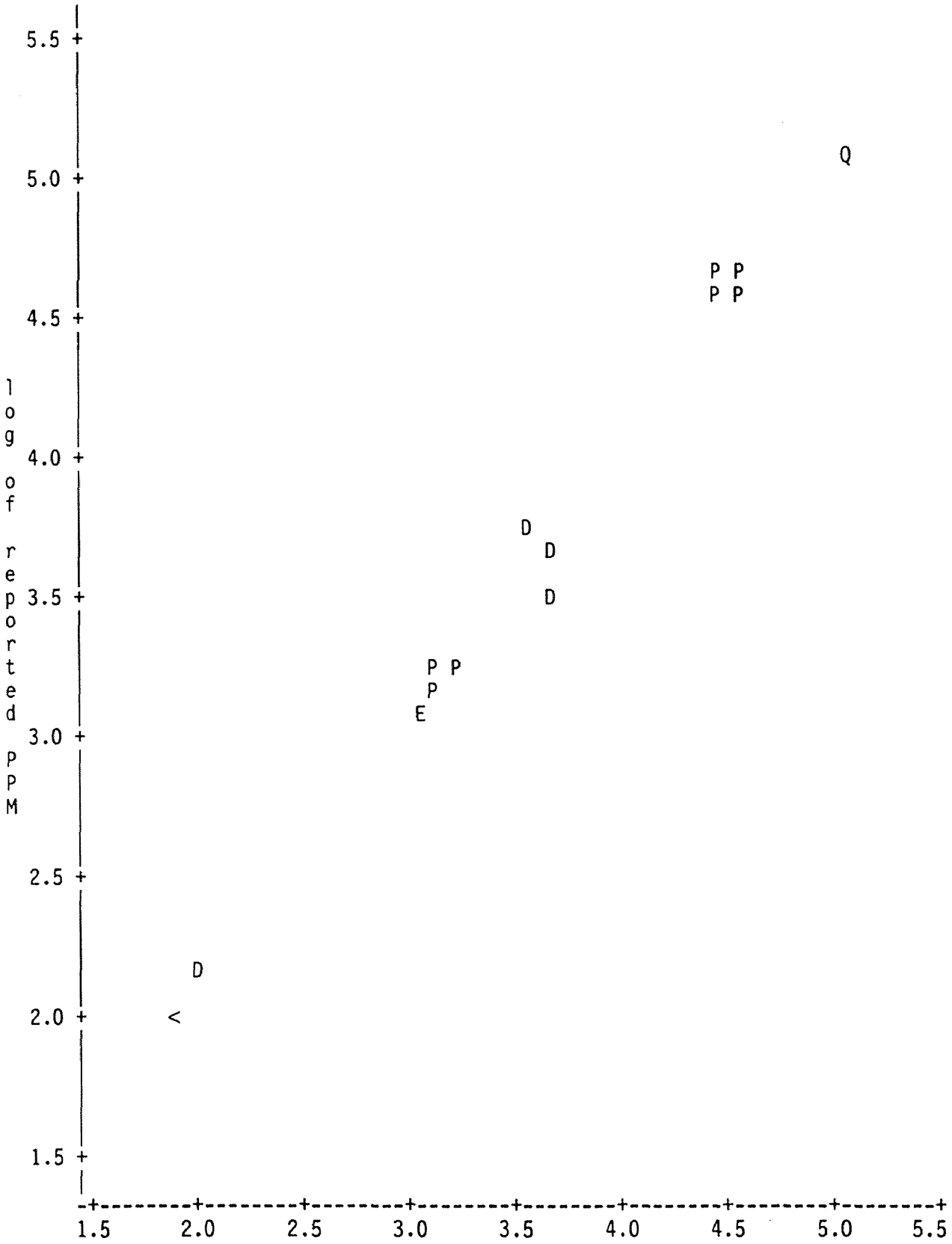
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 2 obs hidden.

---------- METH=4 LAB=41 ----------

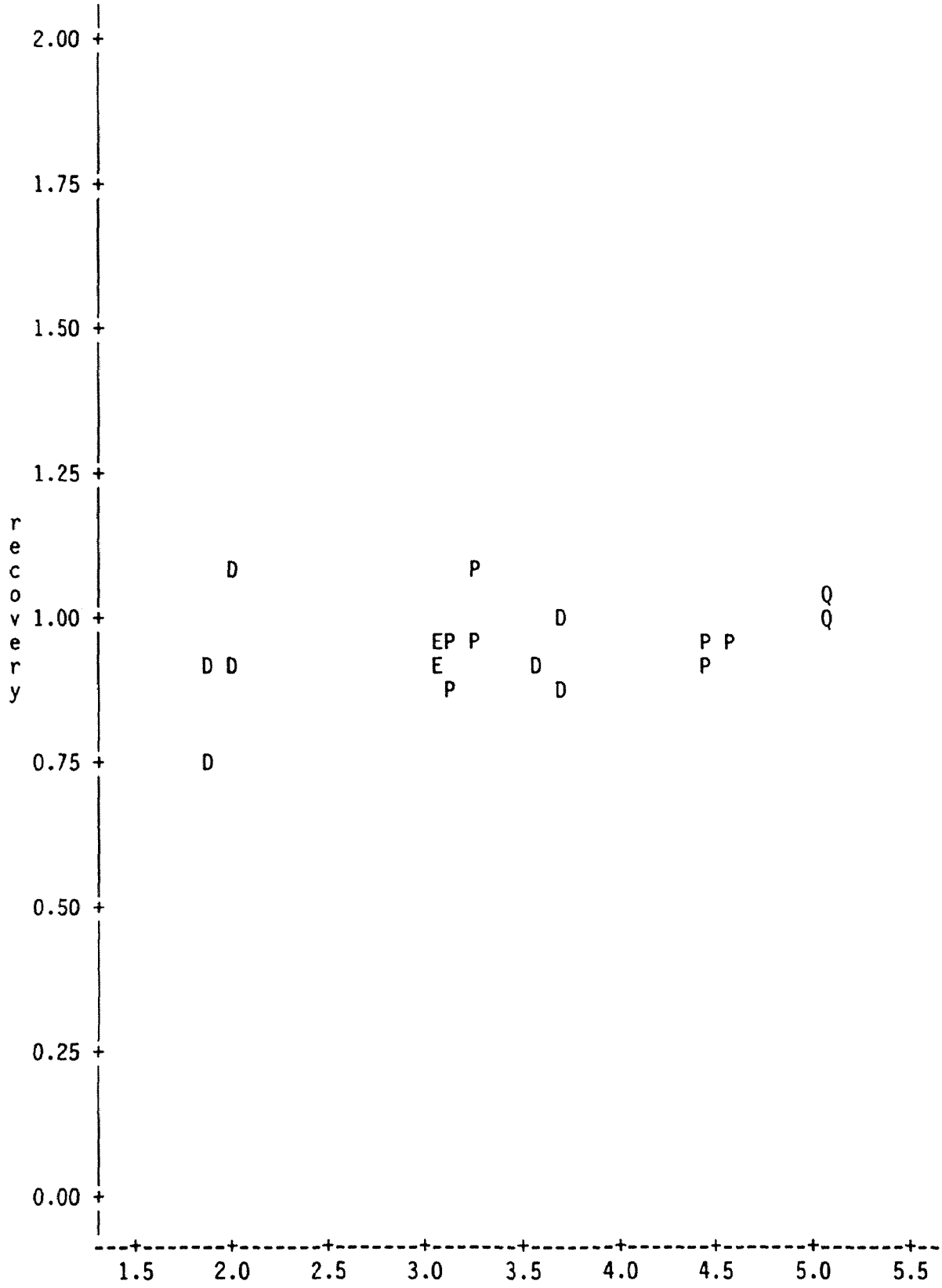
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 6 obs hidden.

---------- METH=4 LAB=42 ----------

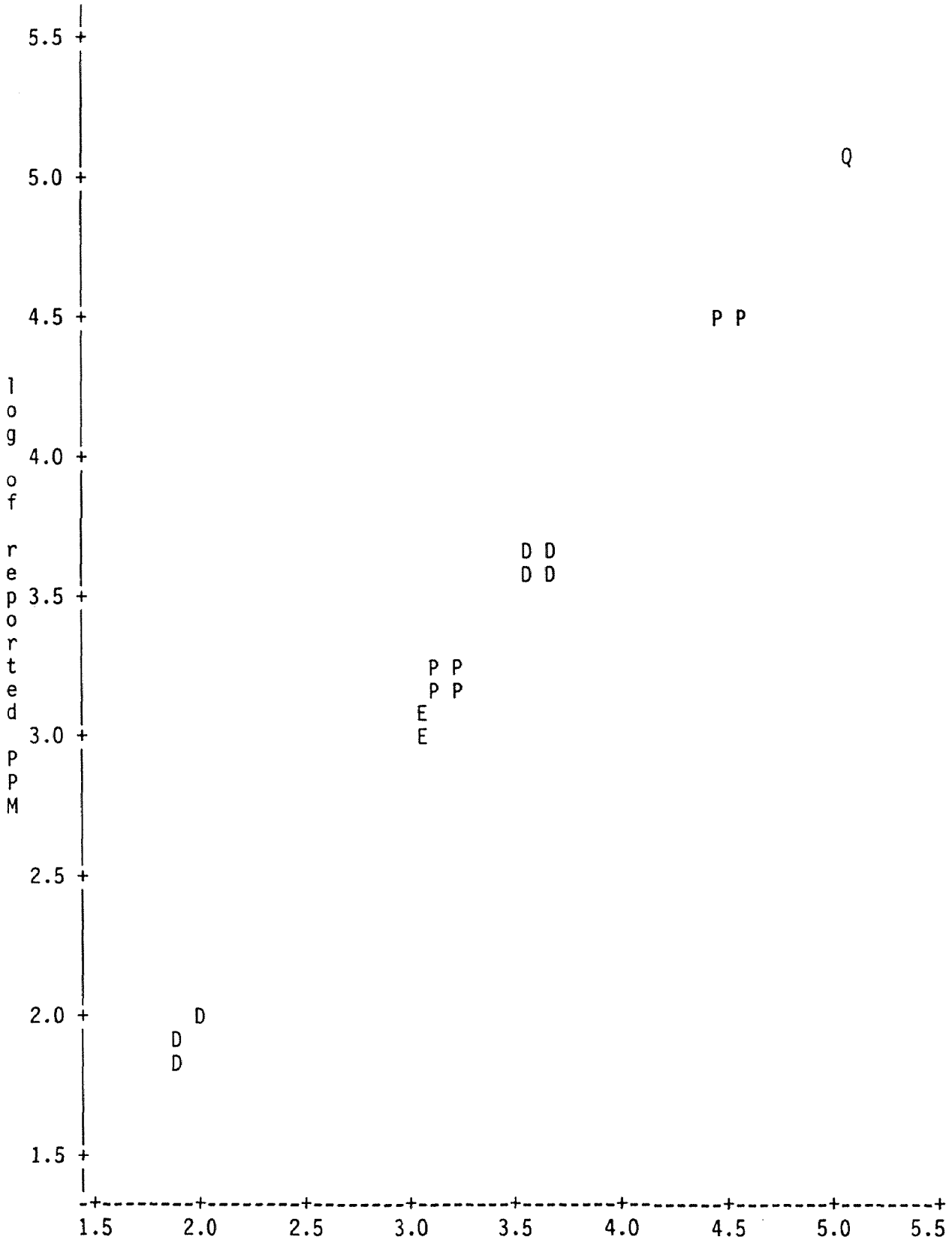
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 2 obs hidden.

---------- METH=4 LAB=42 ----------

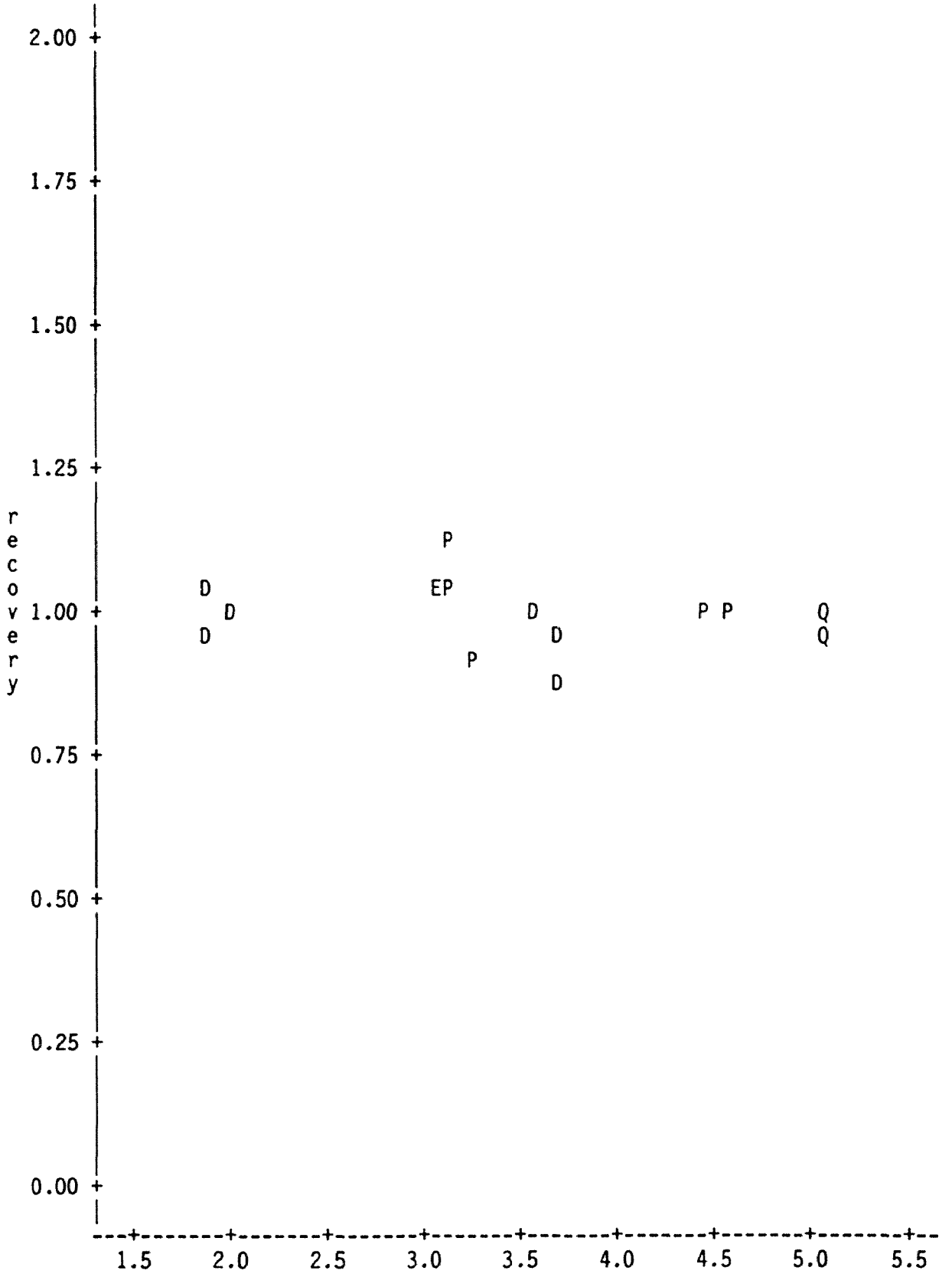
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 4 obs hidden.

---------- METH=4 LAB=43 ----------

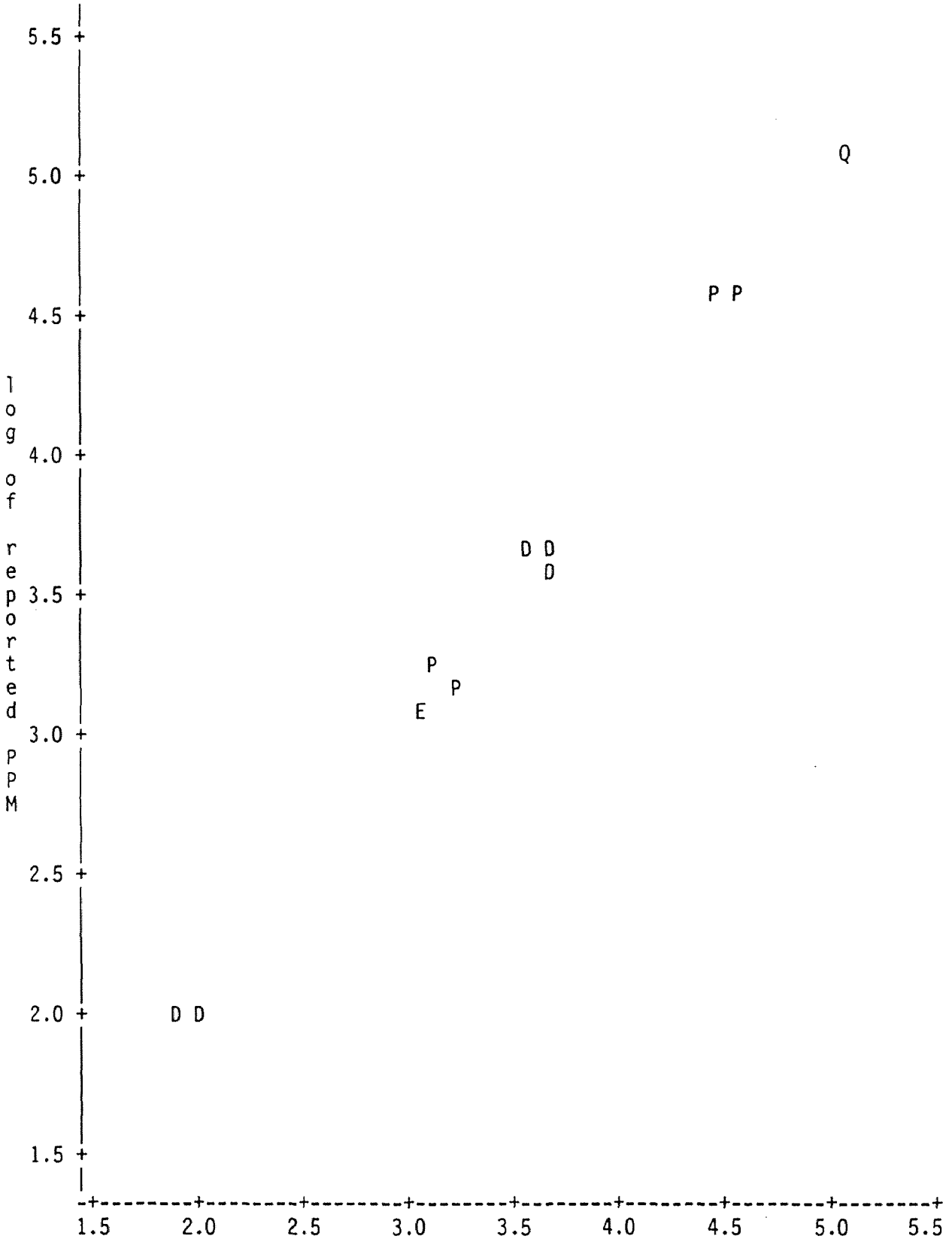
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 6 obs hidden.

---------- METH=4 LAB=43 ----------

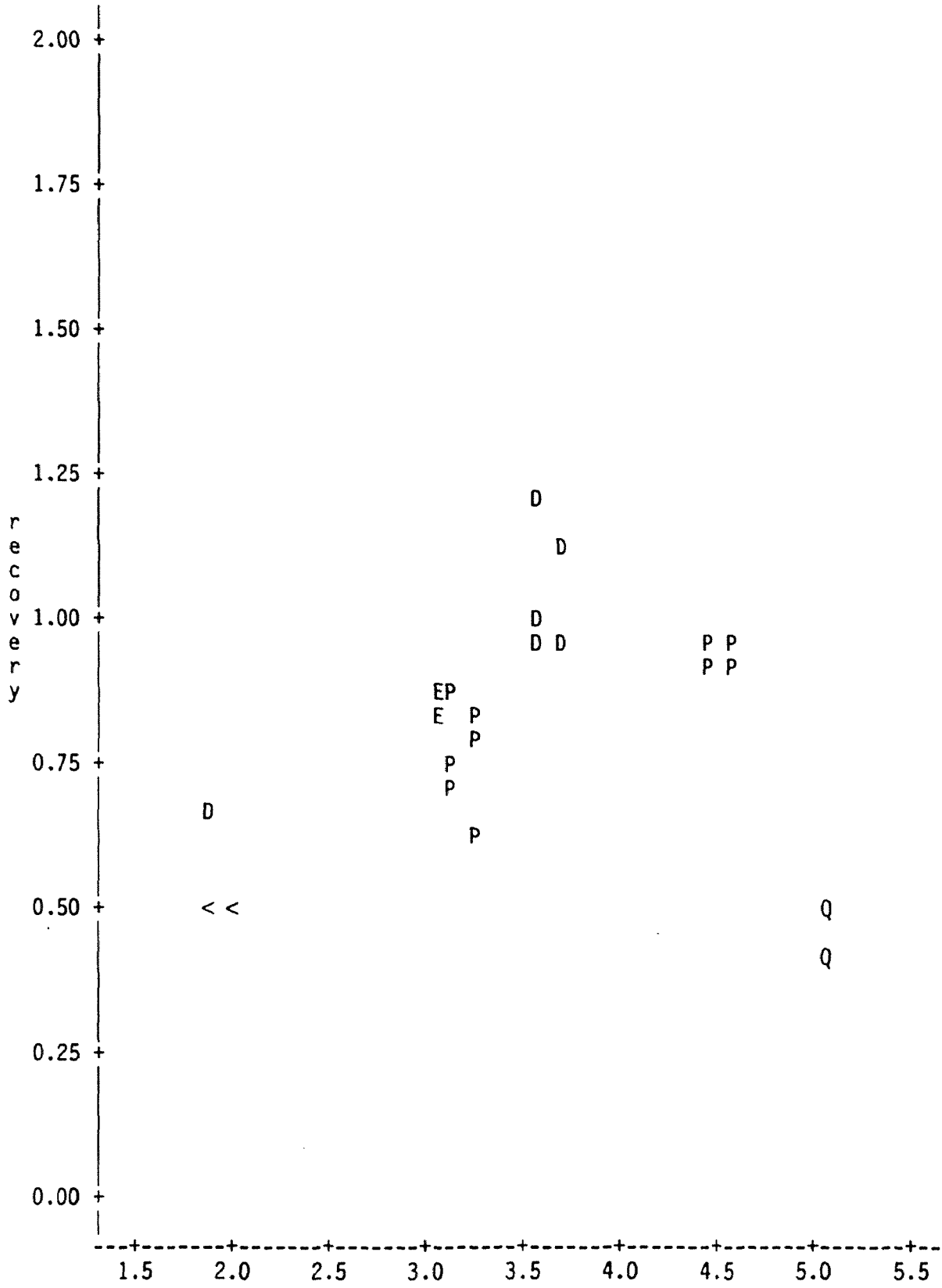
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 9 obs hidden.

---------- METH=4 LAB=44 ----------

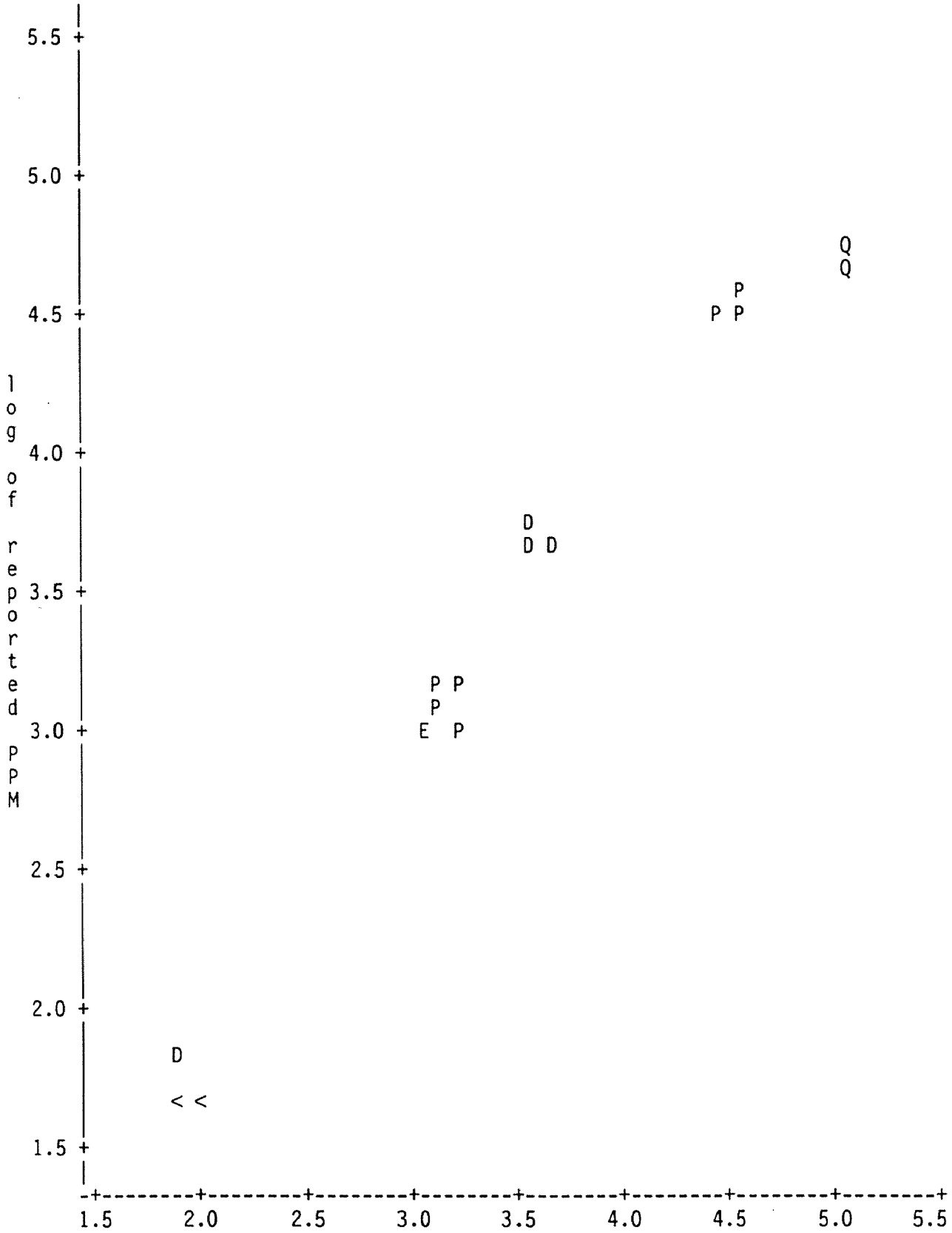
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 8 obs hidden.

---------- METH=4 LAB=44 ----------

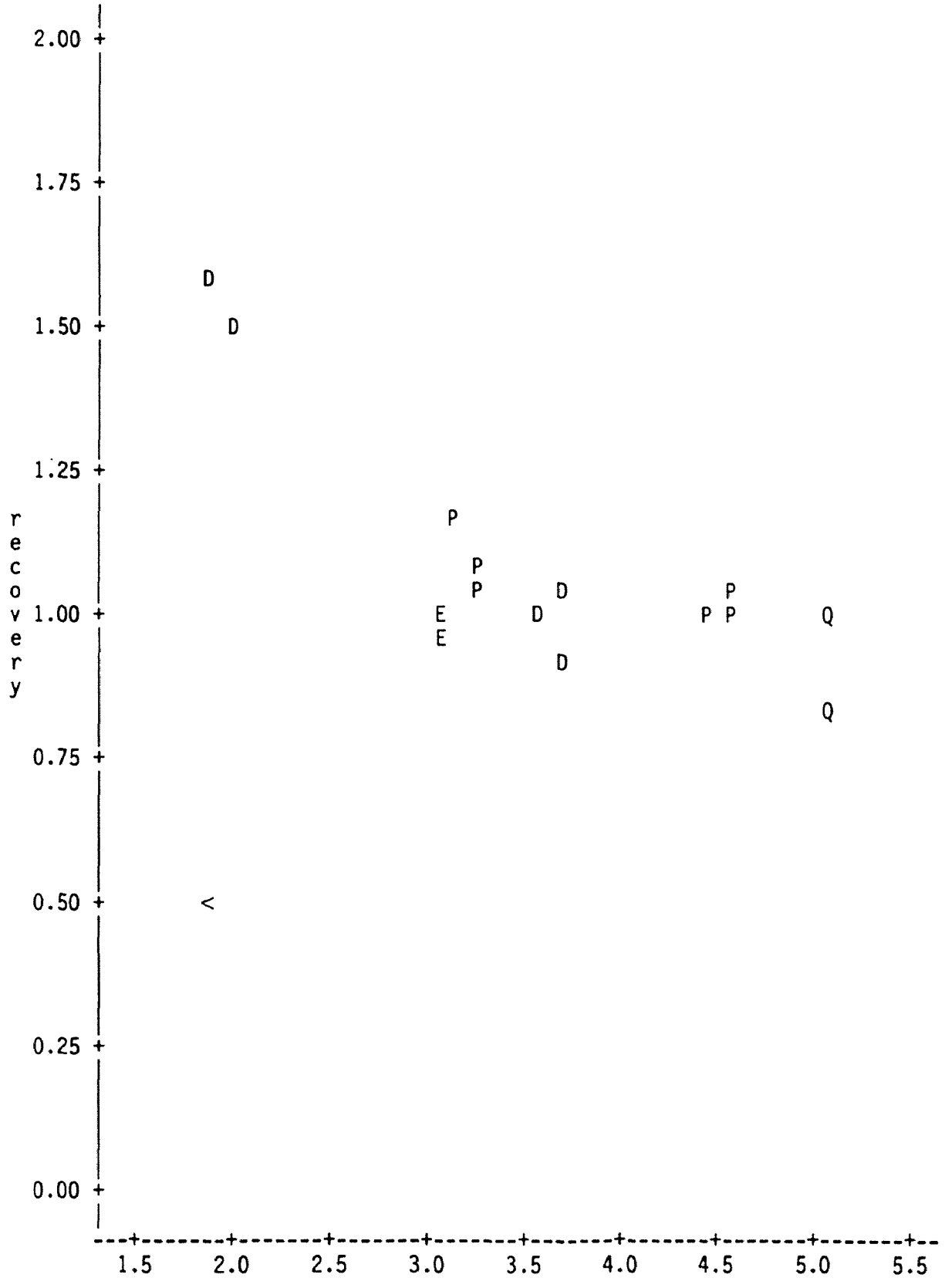
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 14 obs hidden.

---------- METH=4 LAB=45 ----------

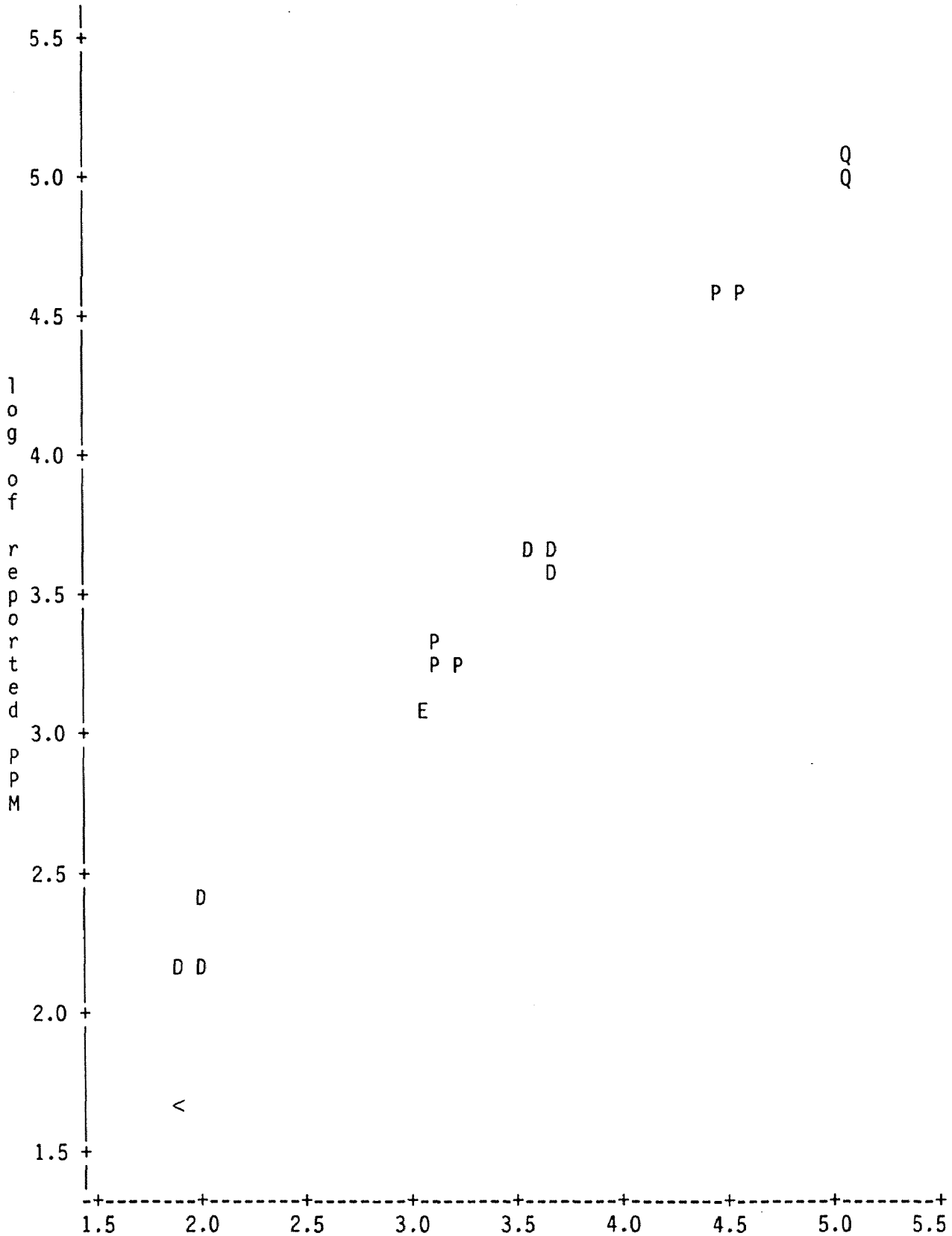
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 3 obs hidden.

---------- METH=4 LAB=45 ----------

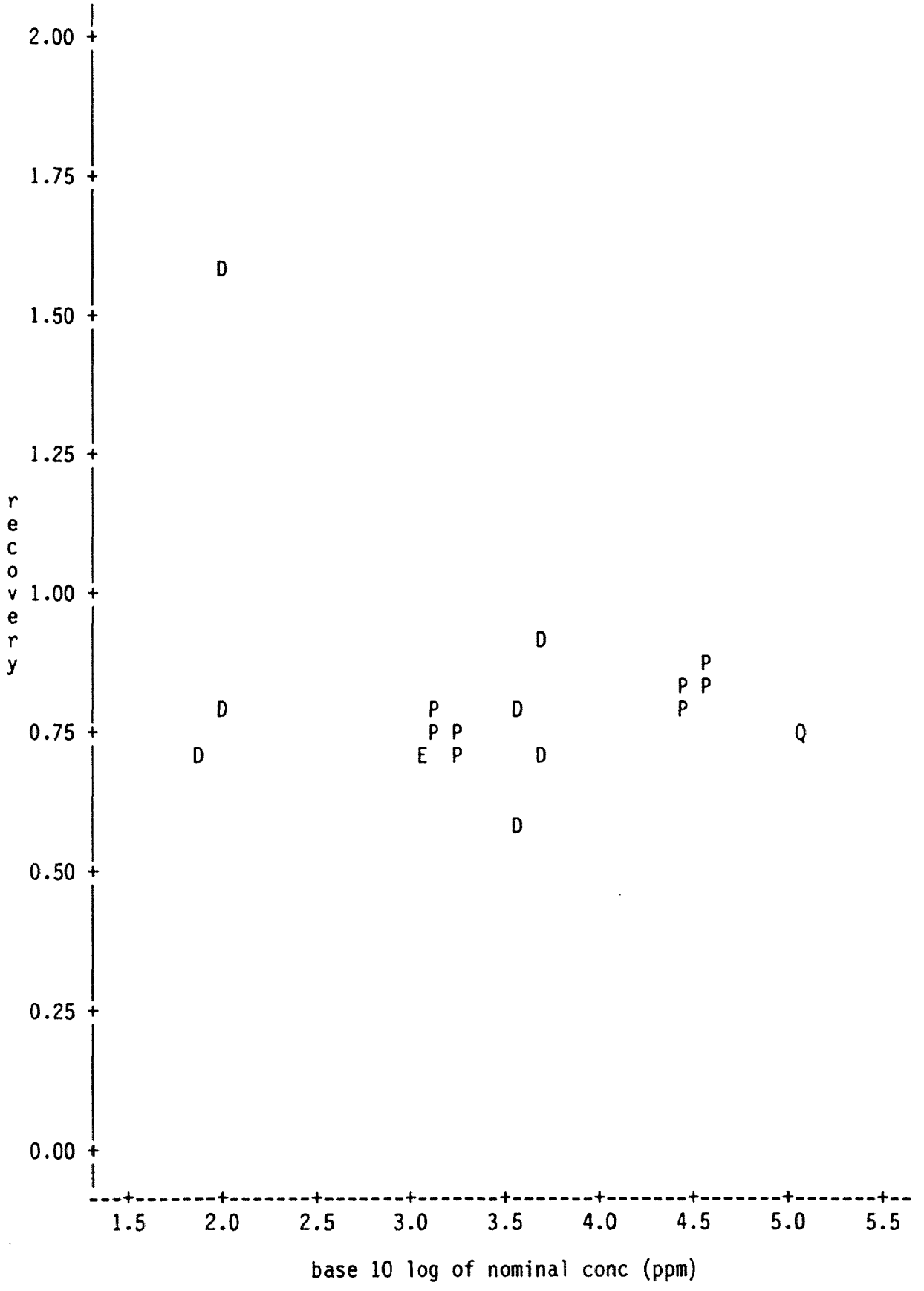
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 5 obs hidden.

---------- METH=4 LAB=46 ----------

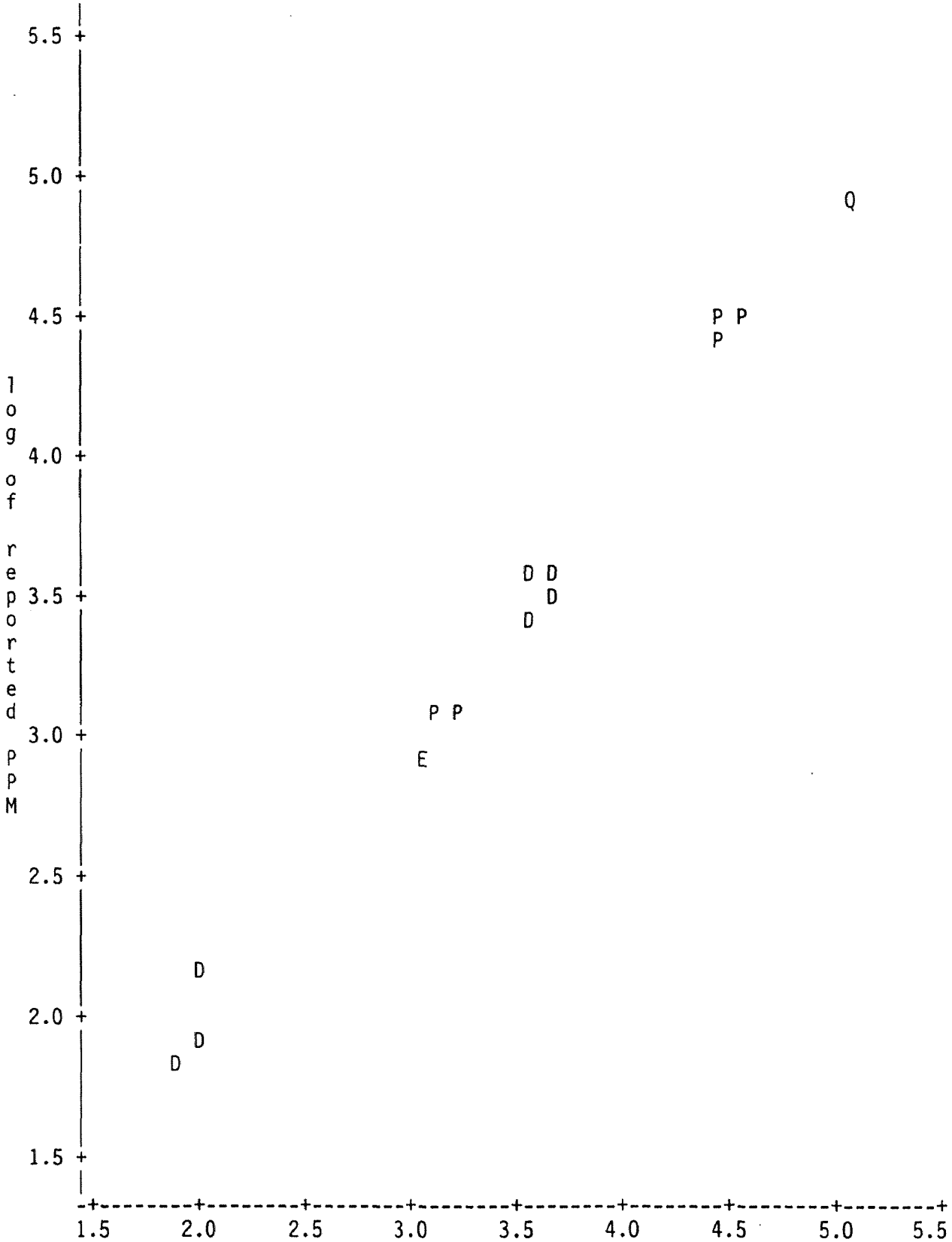
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 2 obs hidden.

---------- METH=4 LAB=46 ----------

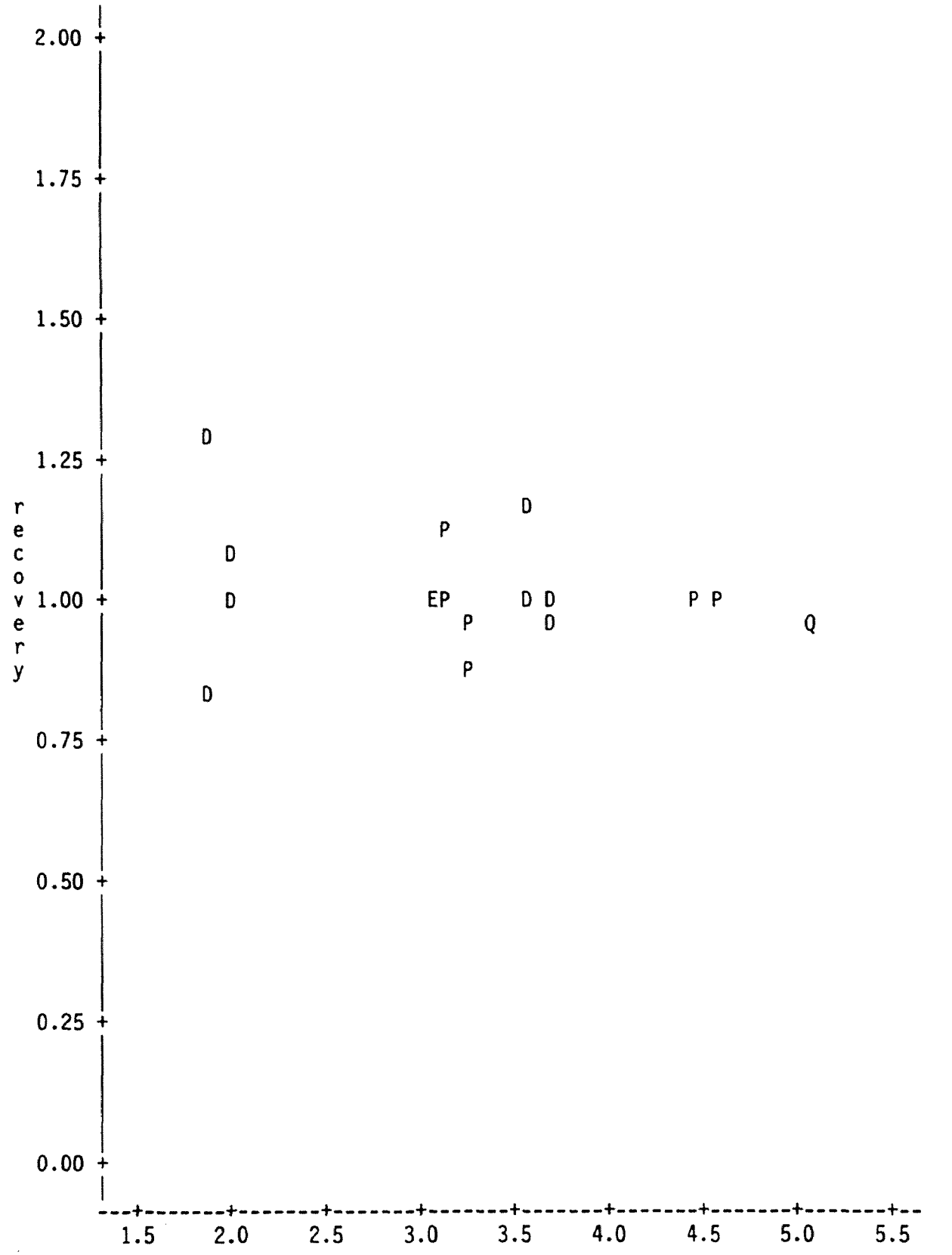
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 5 obs hidden.

---------- METH=4 LAB=47 ----------

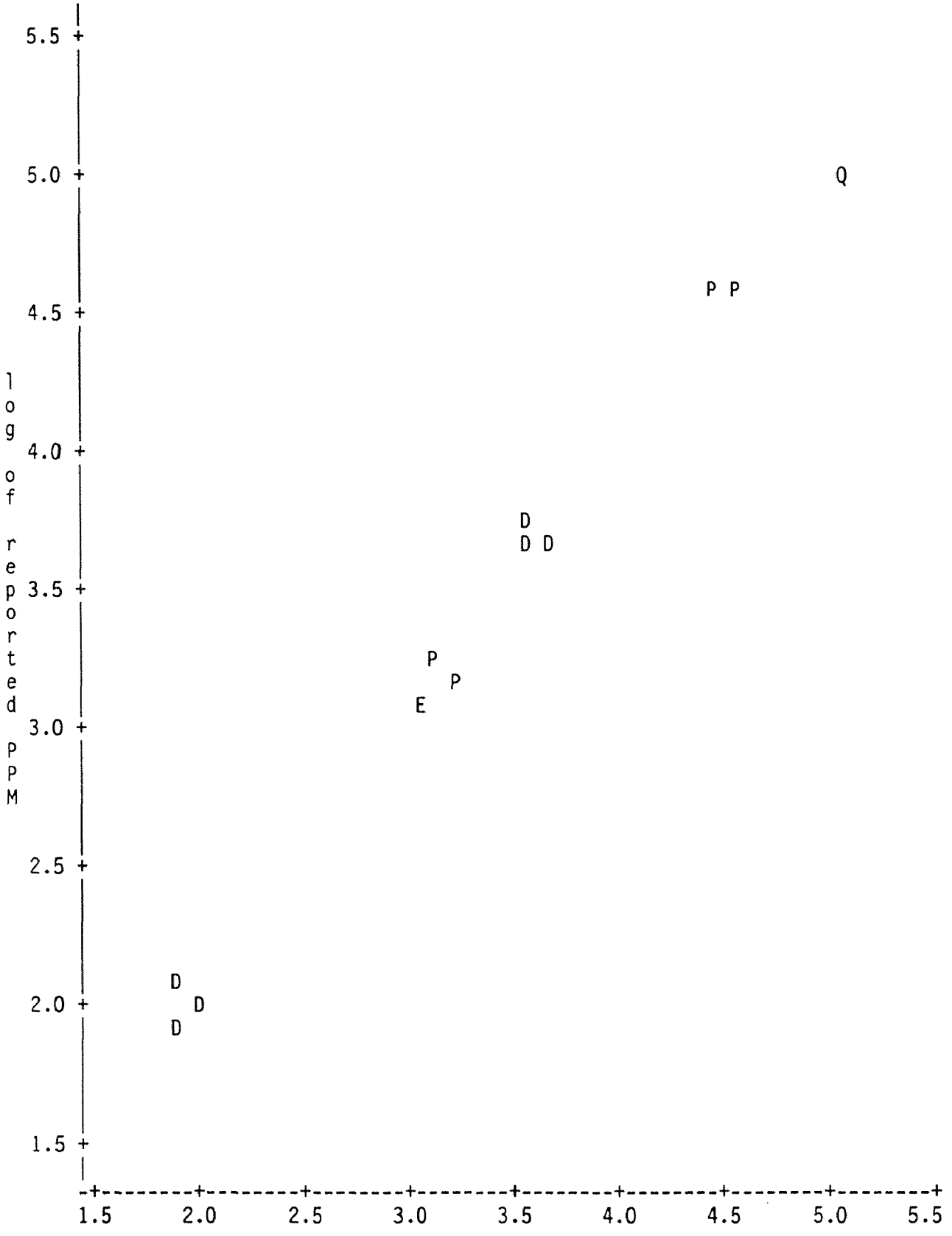
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 4 obs hidden.

---------- METH=4 LAB=47 ----------

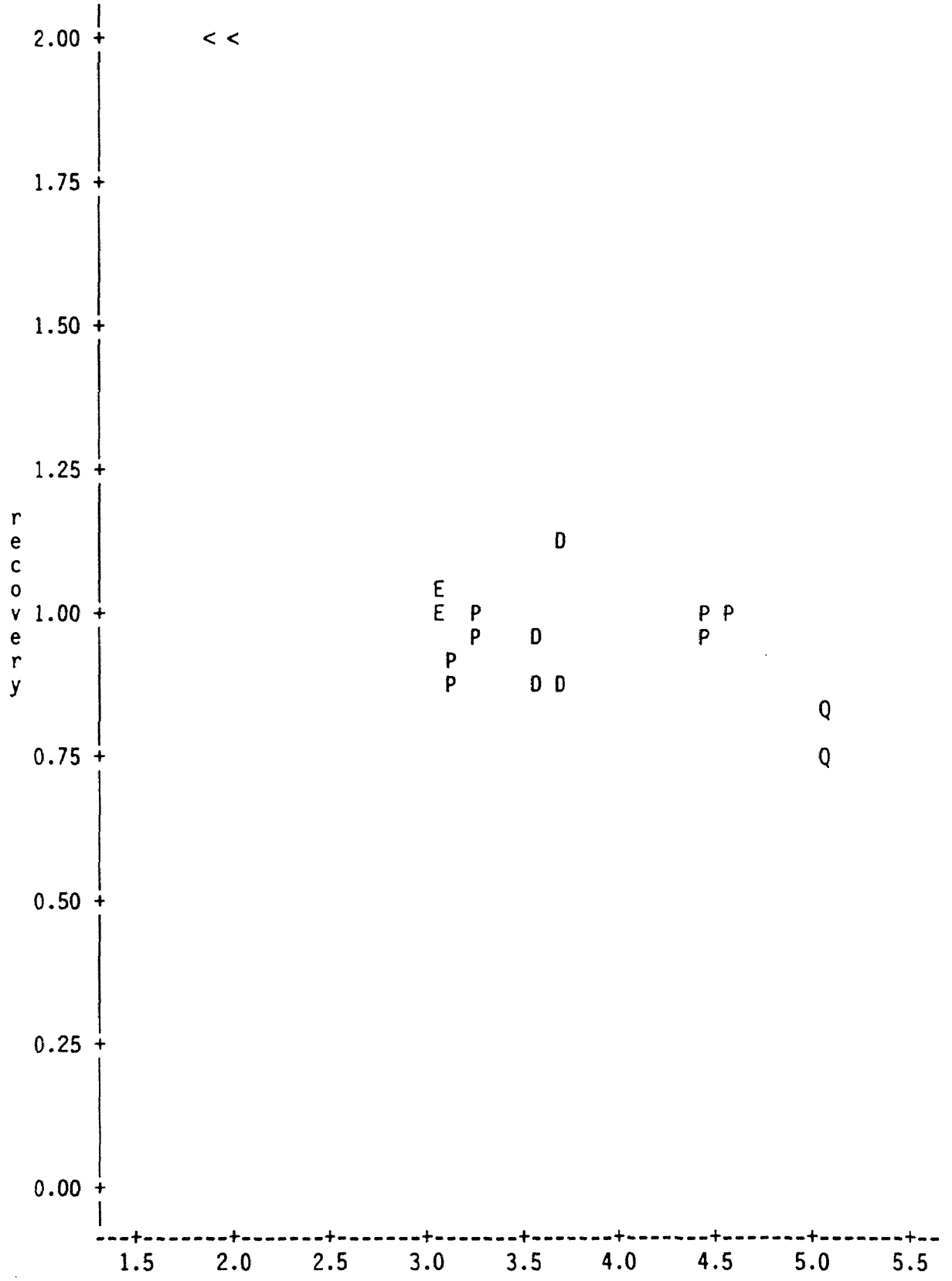
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 8 obs hidden.

---------- METH=4 LAB=48 ----------

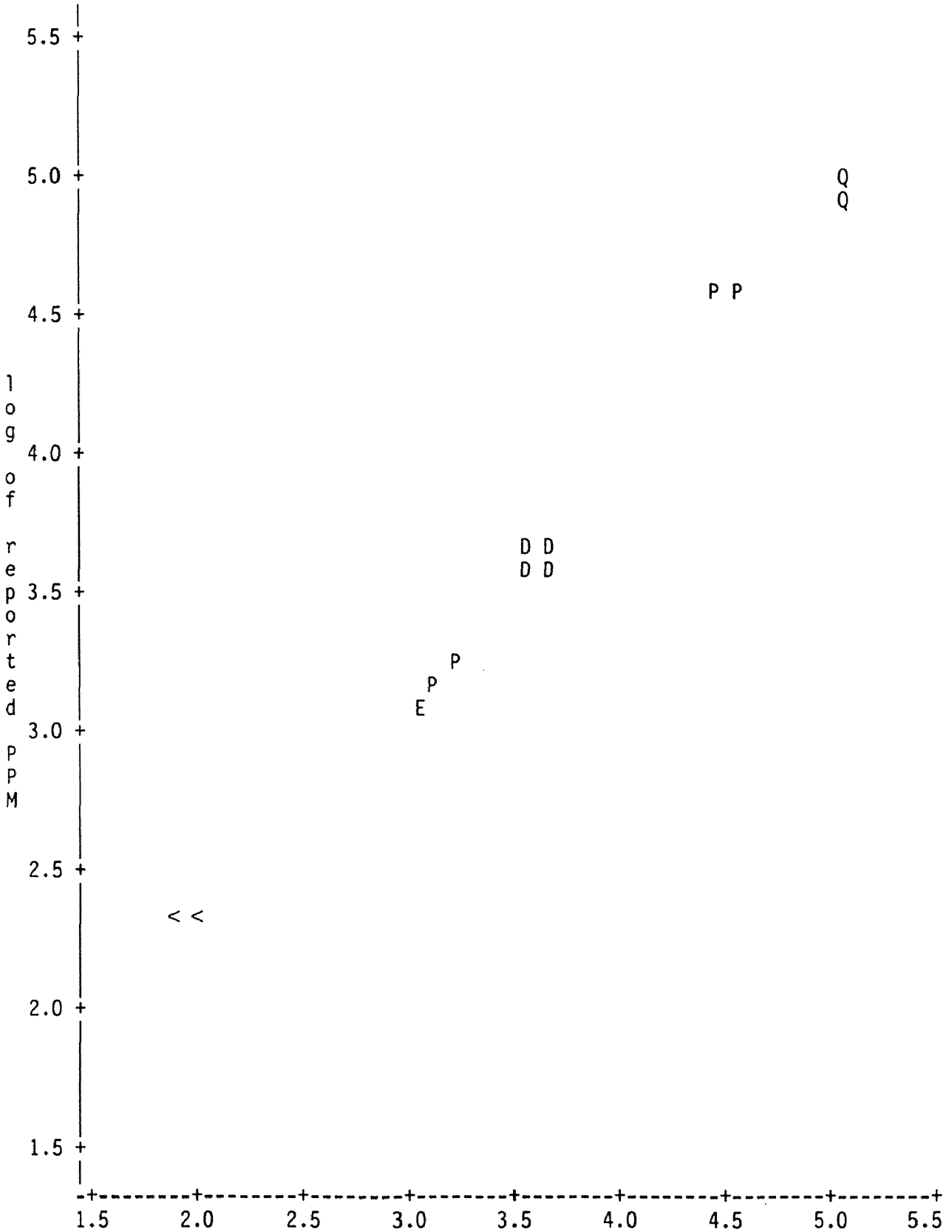
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 3 obs hidden.

---------- METH=4 LAB=48 ----------

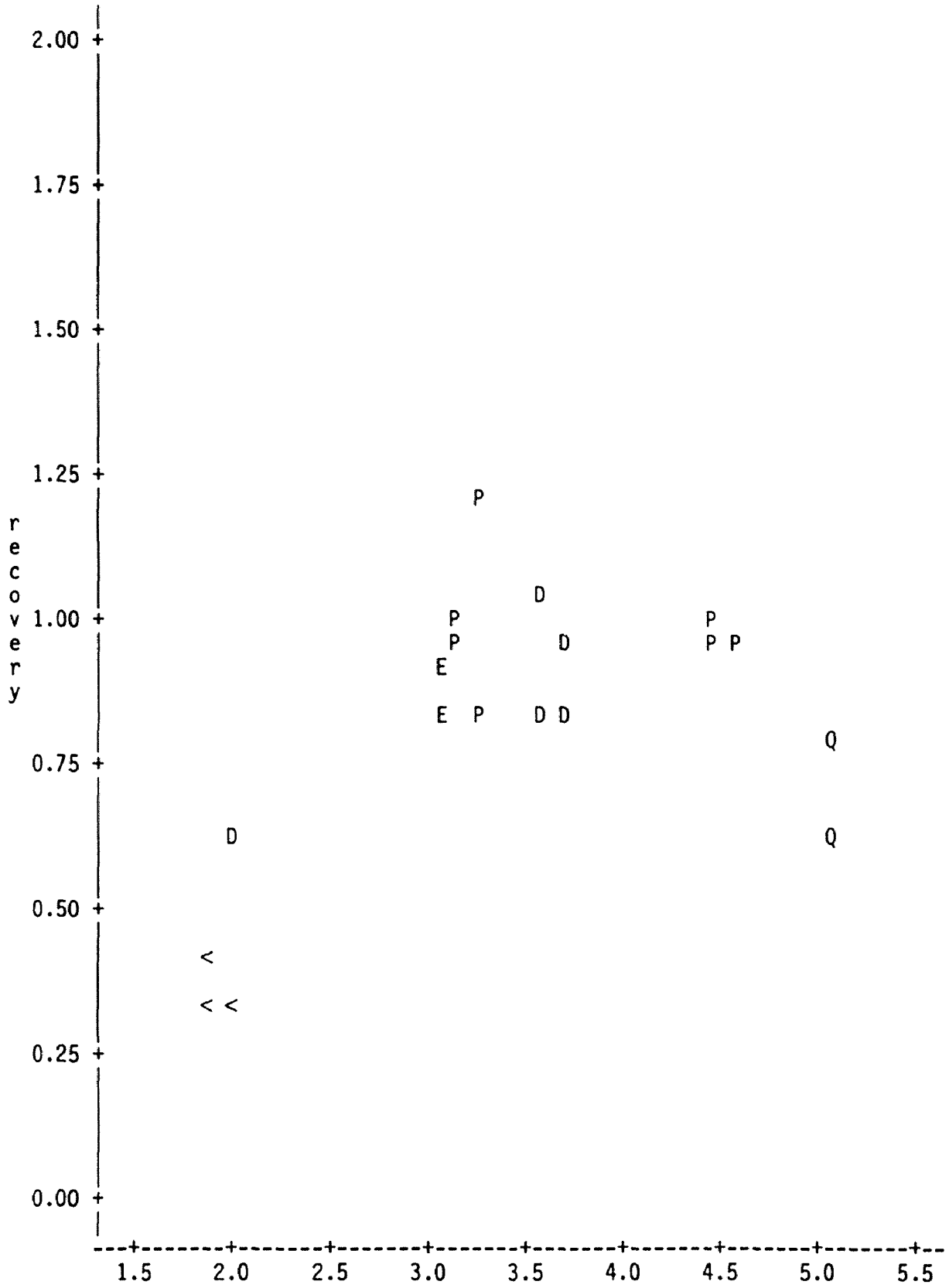
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 7 obs hidden.

---------- METH=4 LAB=49 ----------

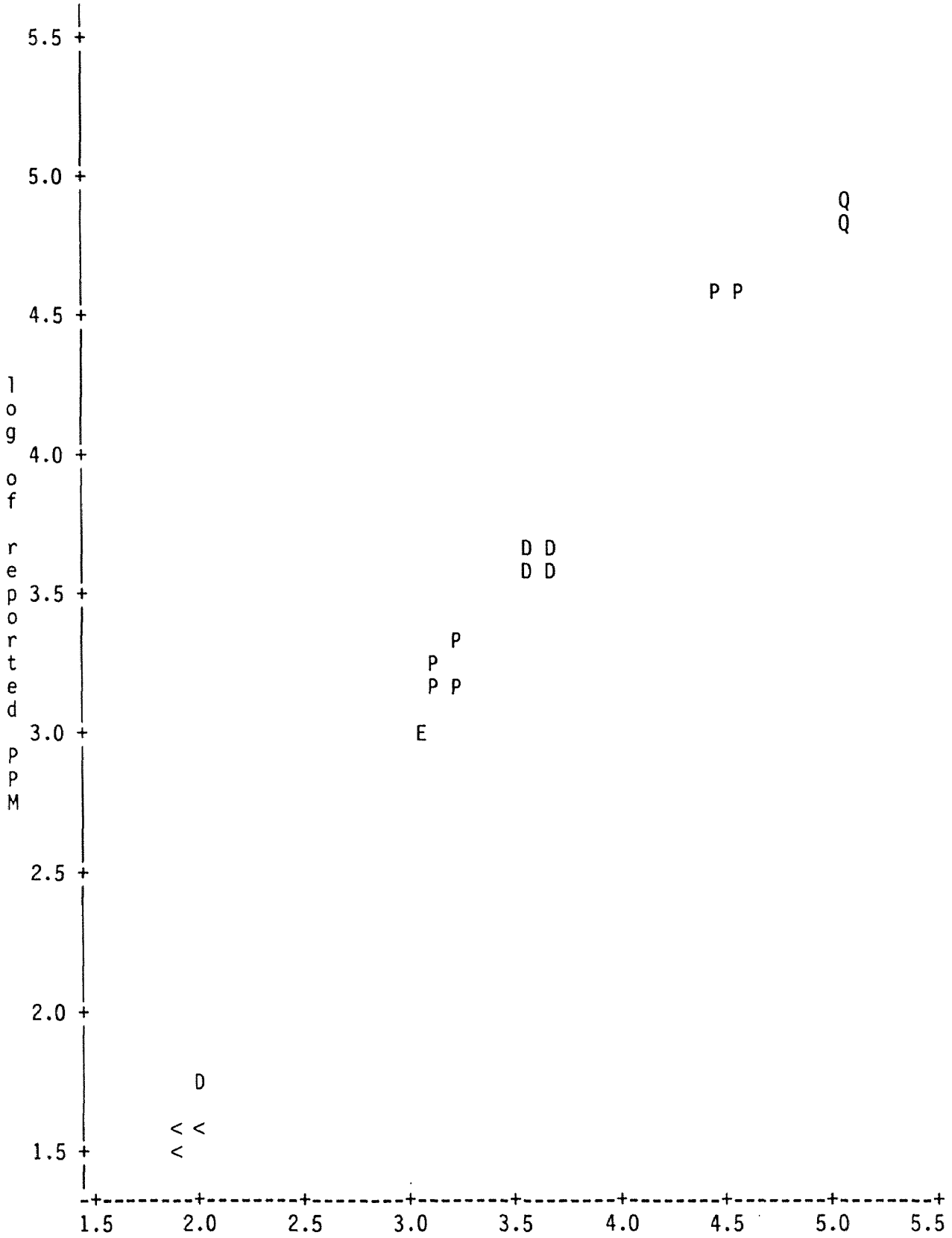
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 1 obs hidden.

---------- METH=4 LAB=49 ----------

Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



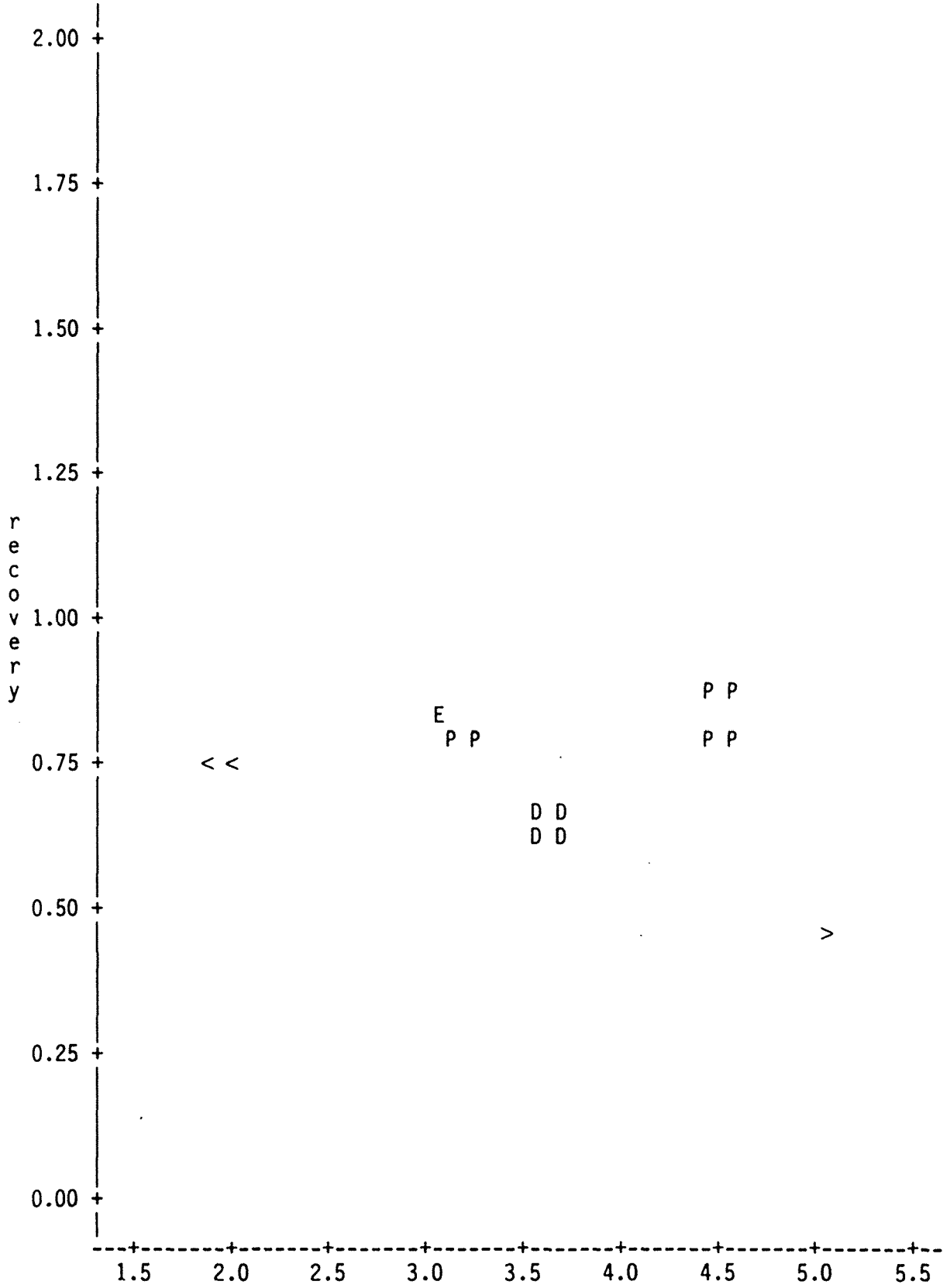
NOTE: 3 obs hidden.

Appendix G-7-5

Laboratory XRF Laboratories

---------- METH=5 LAB=50 ----------

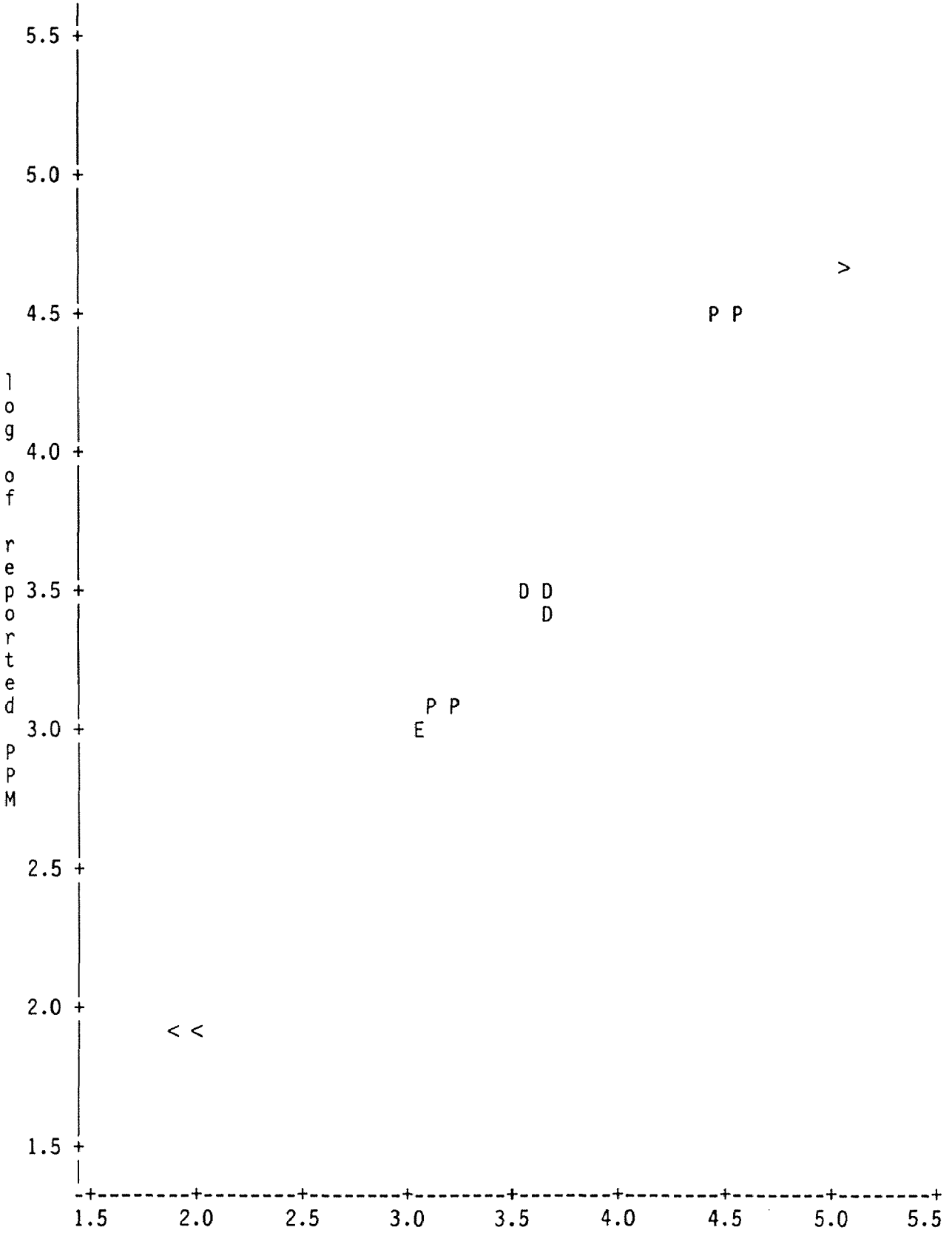
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 6 obs hidden.

---------- METH=5 LAB=50 ----------

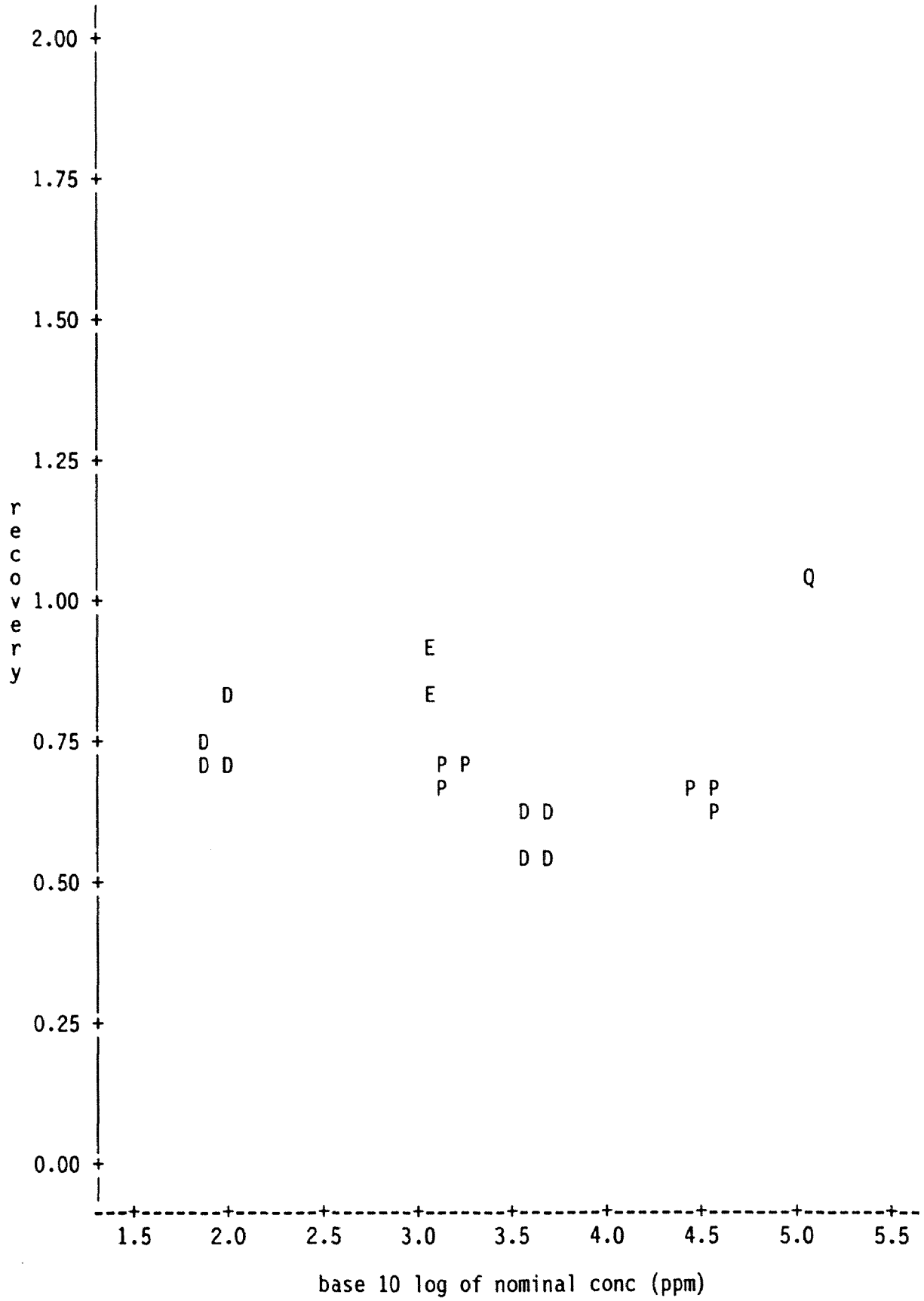
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 9 obs hidden.

---------- METH=5 LAB=51 ----------

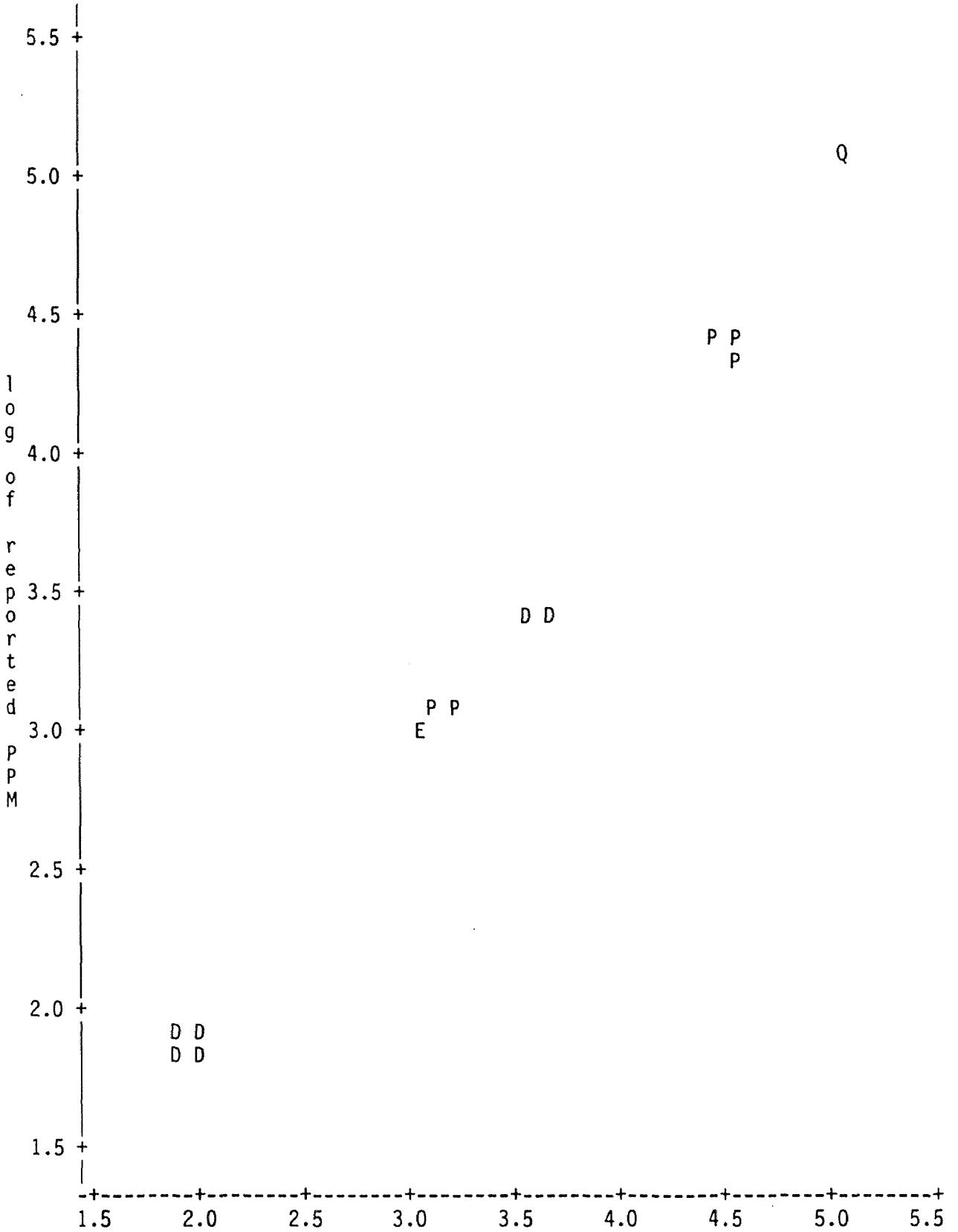
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 3 obs hidden.

---------- METH=5 LAB=51 ----------

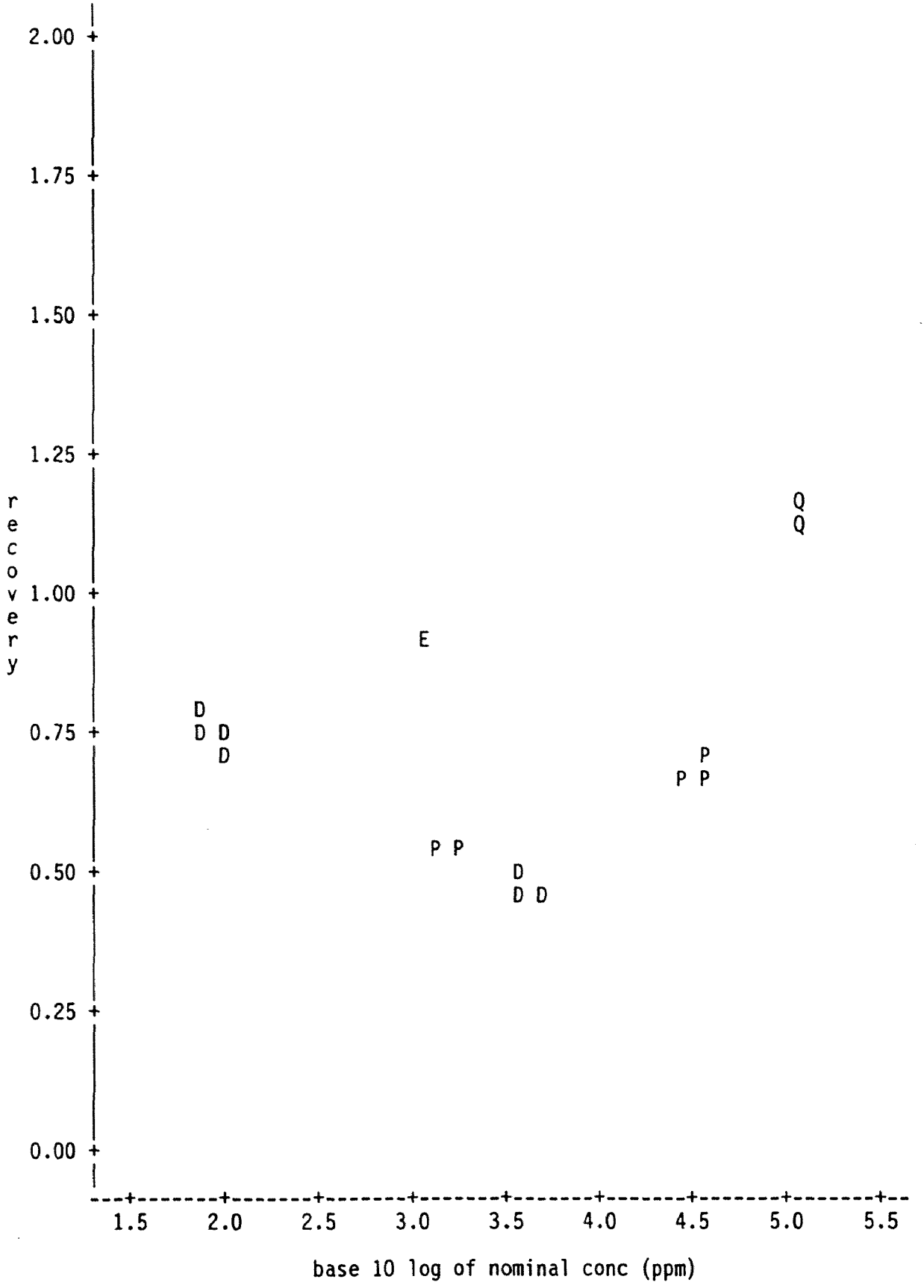
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 7 obs hidden.

---------- METH=5 LAB=52 ----------

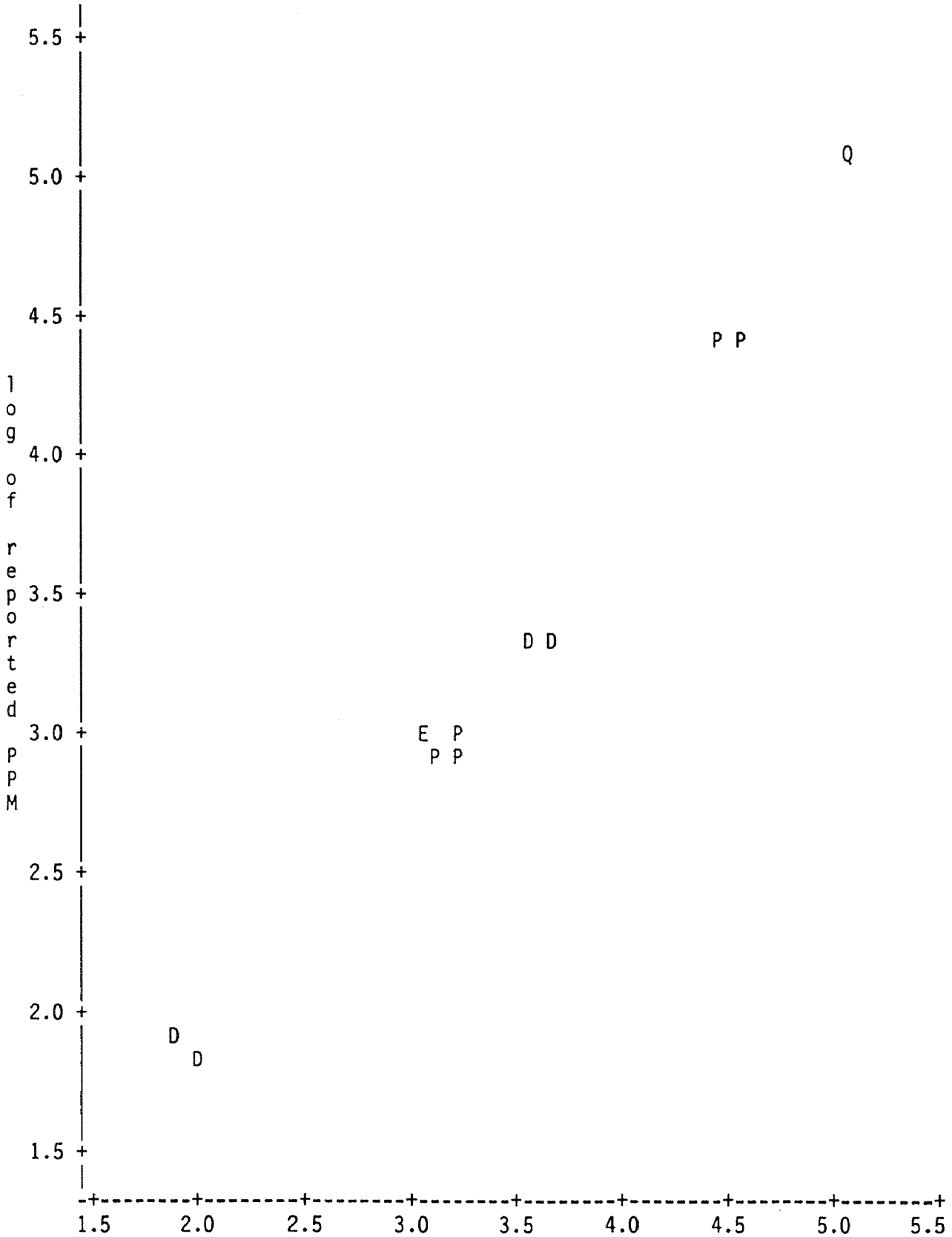
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 5 obs hidden.

---------- METH=5 LAB=52 ----------

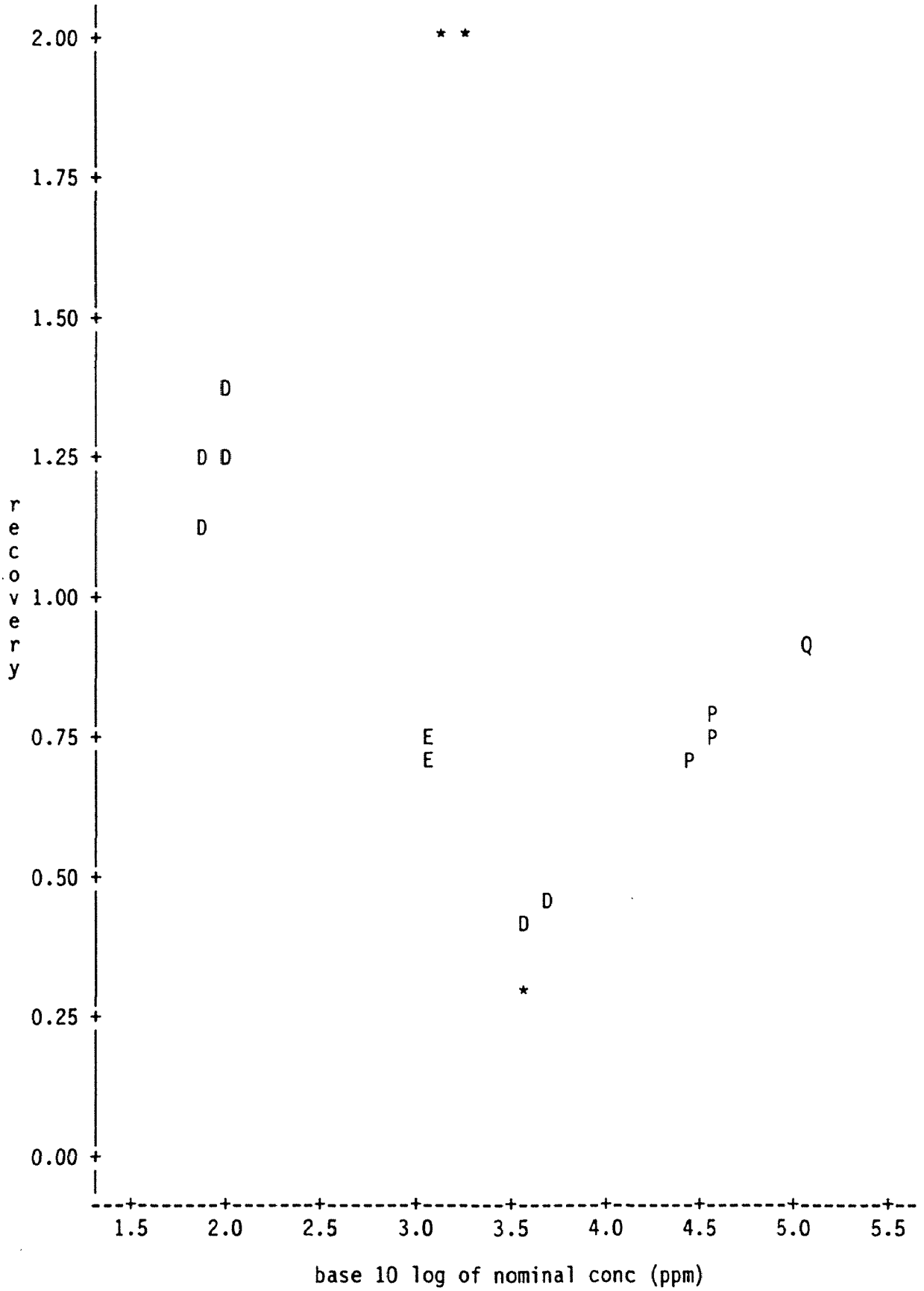
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 9 obs hidden.

---------- METH=5 LAB=53 ----------

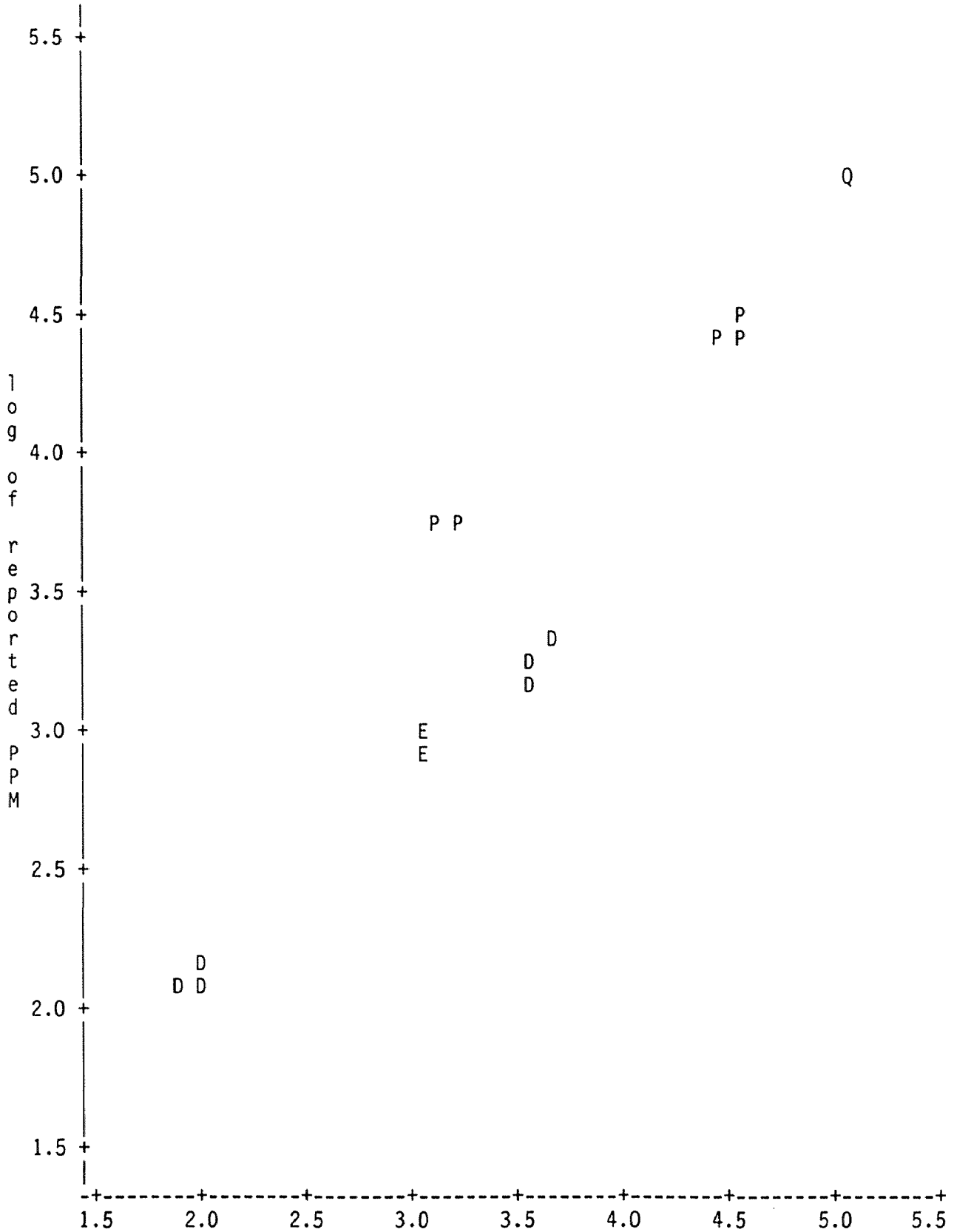
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 5 obs hidden.

---------- METH=5 LAB=53 ----------

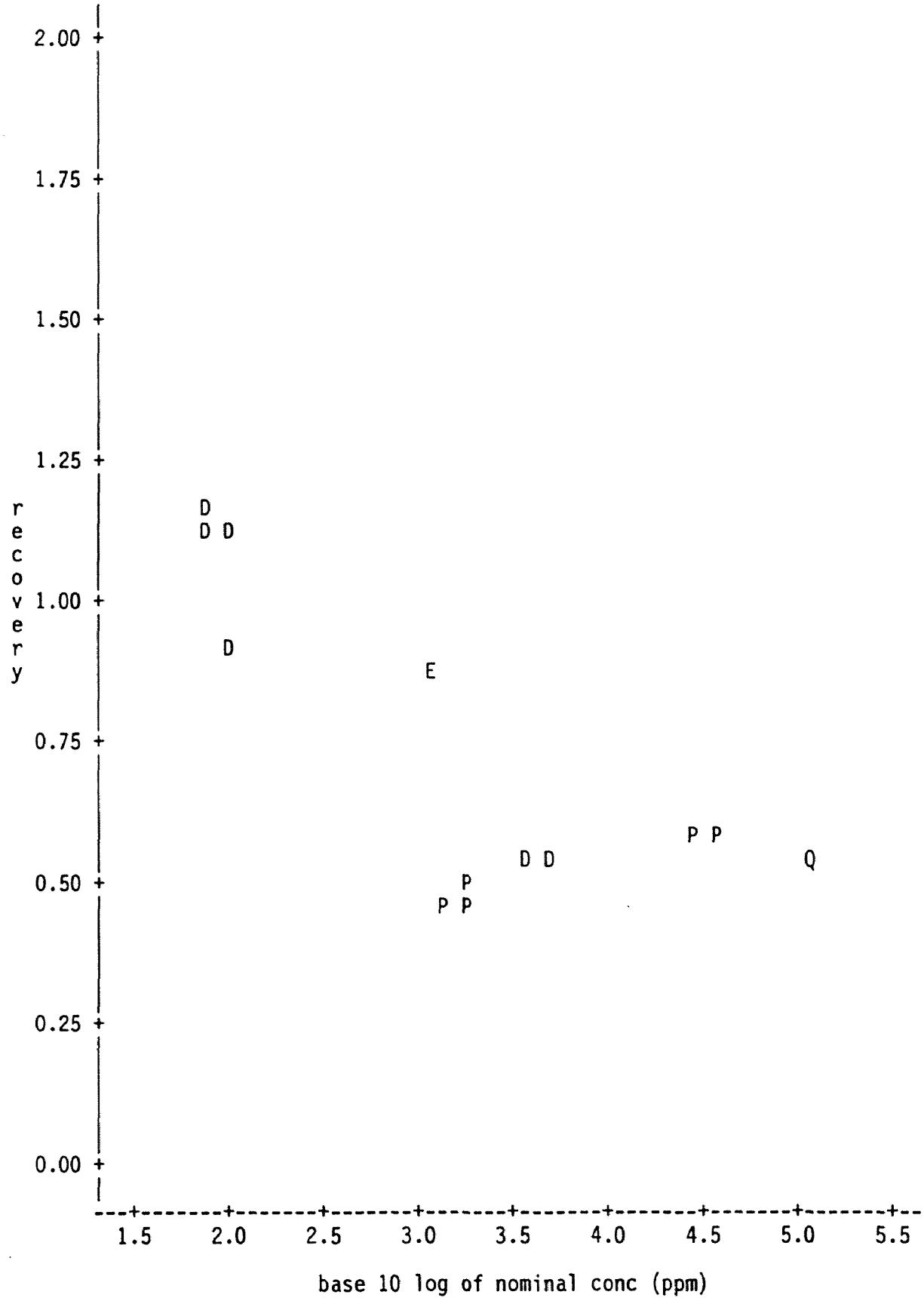
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 6 obs hidden.

---------- METH=5 LAB=54 ----------

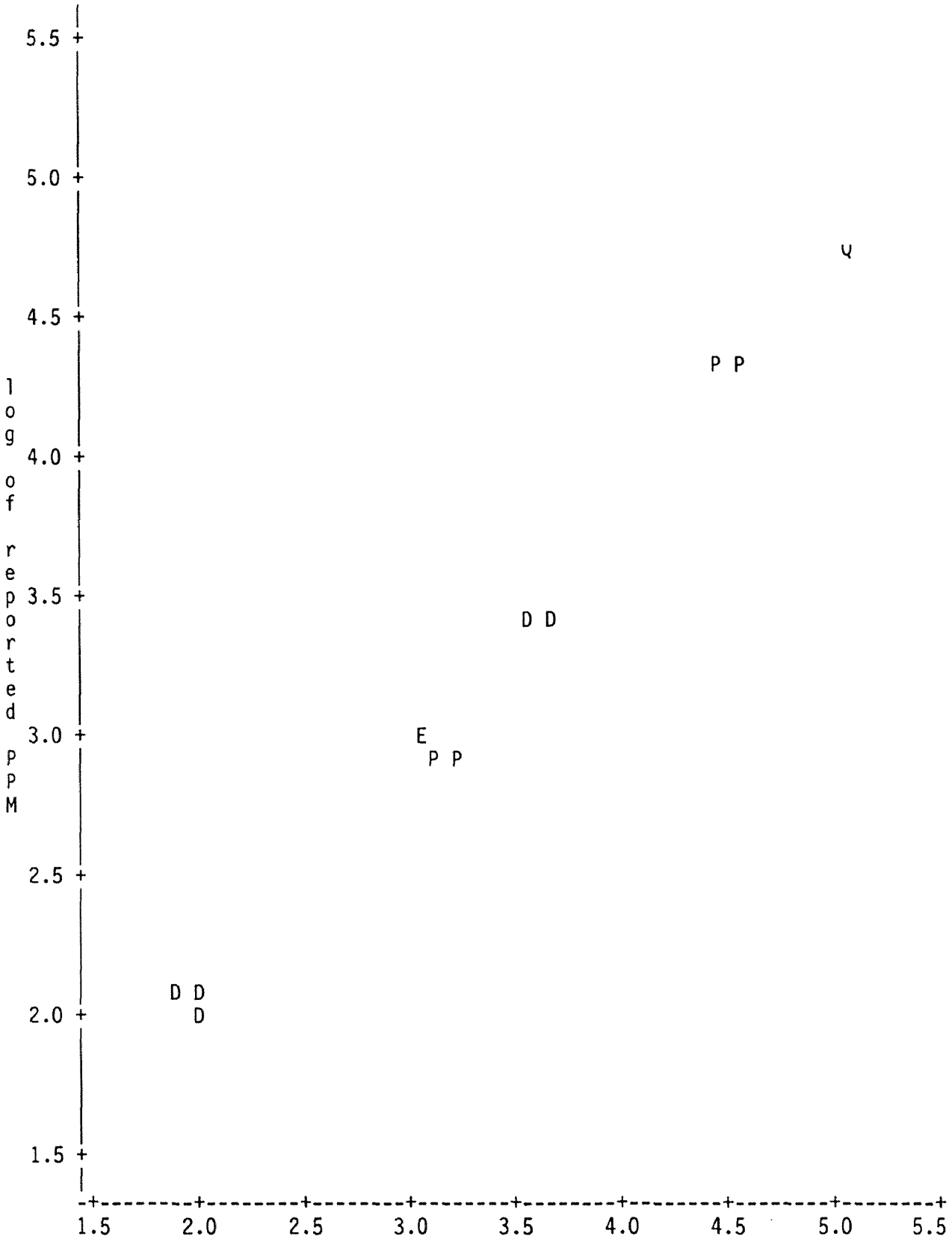
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 7 obs hidden.

---------- METH=5 LAB=54 ----------

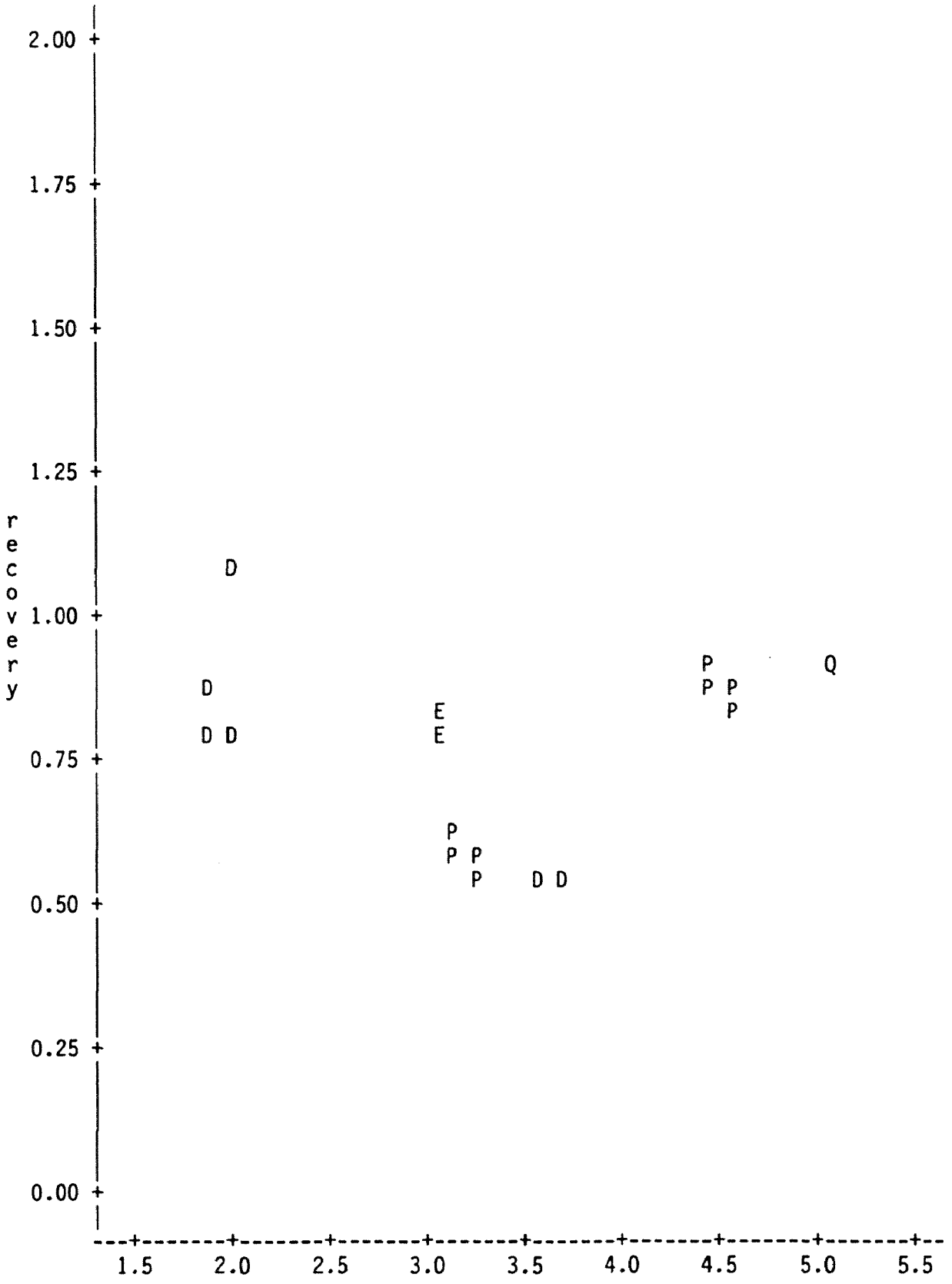
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 9 obs hidden.

---------- METH=5 LAB=55 ----------

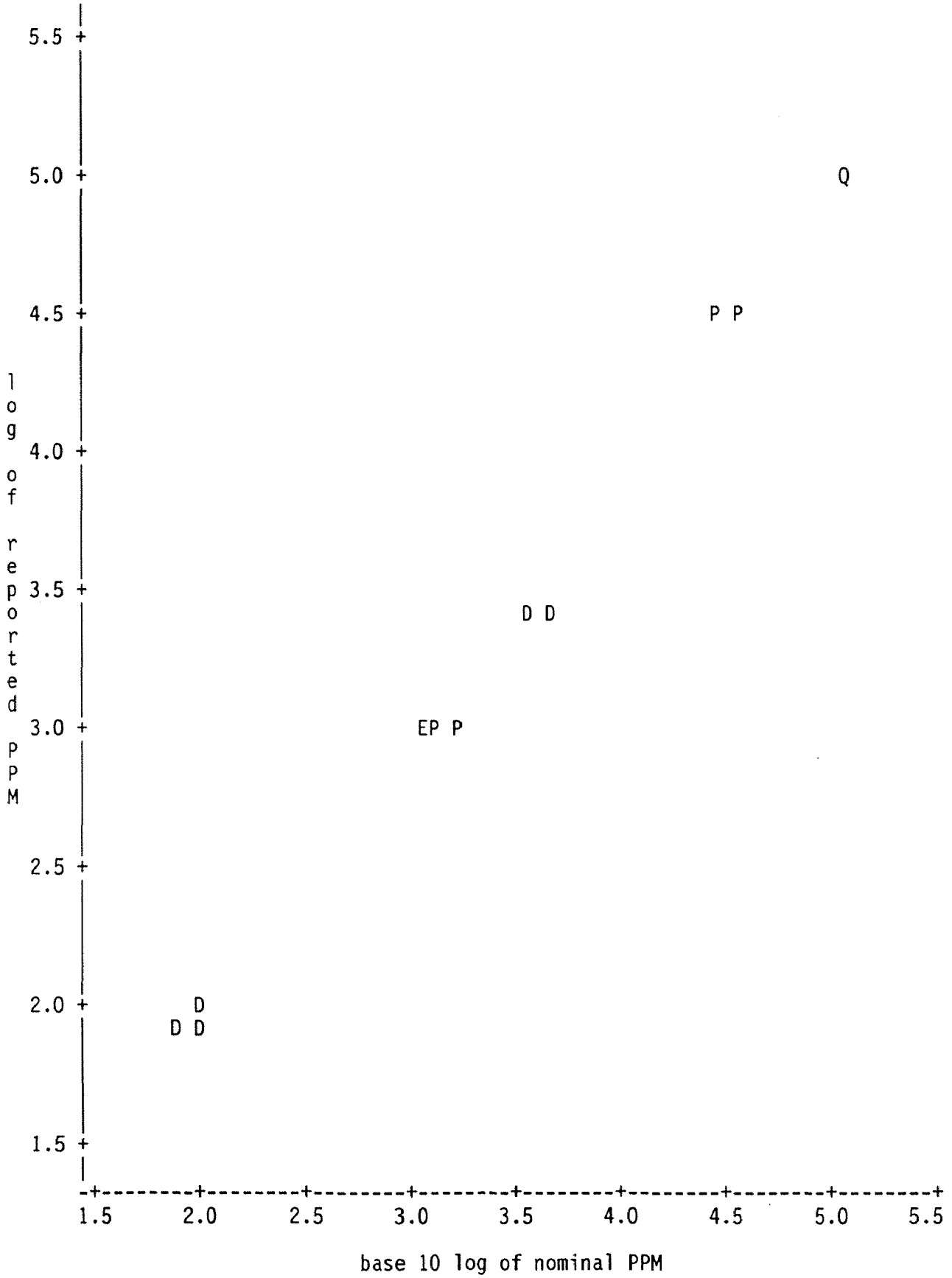
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 3 obs hidden.

---------- METH=5 LAB=55 ----------

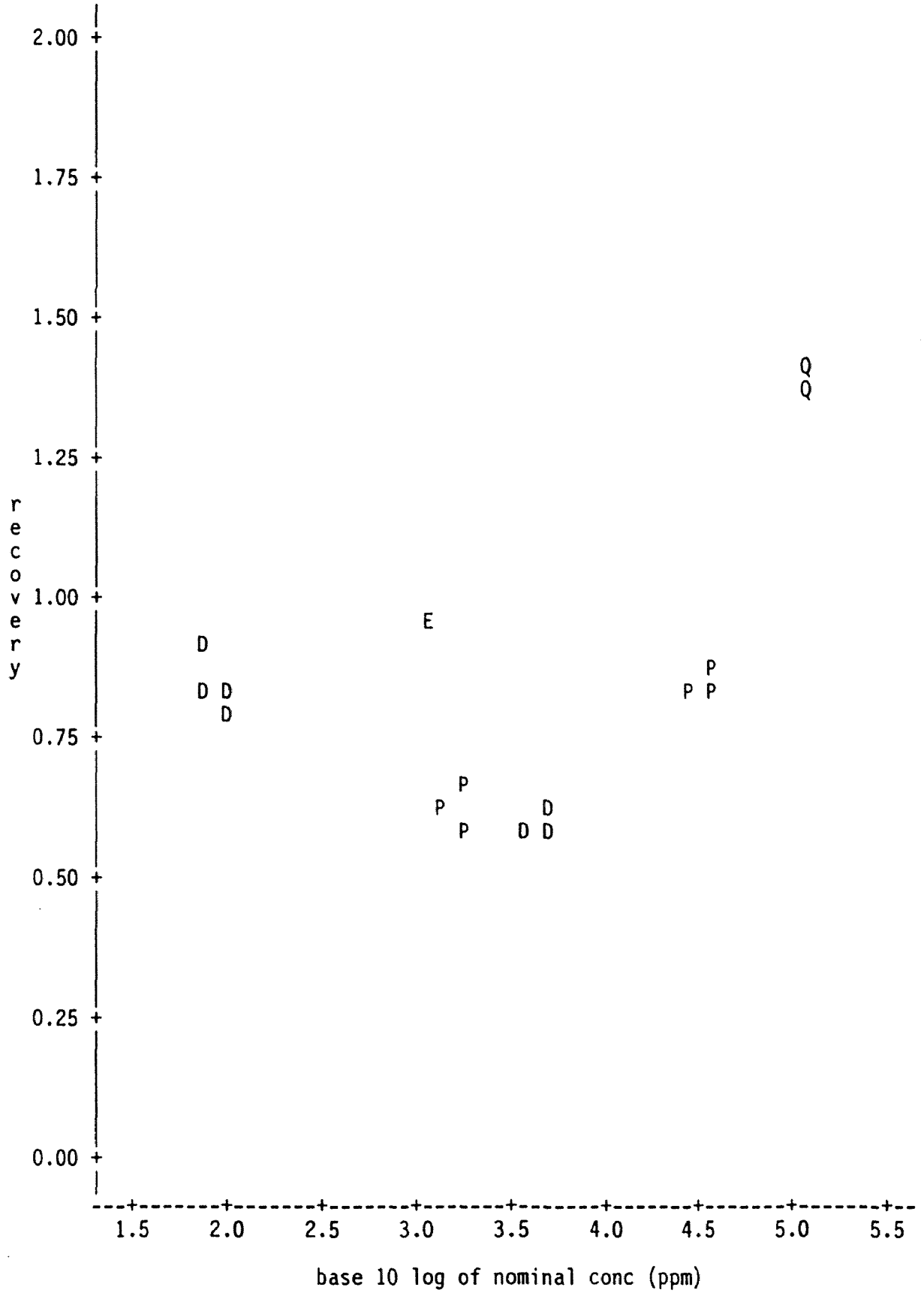
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 9 obs hidden.

---------- METH=5 LAB=56 ----------

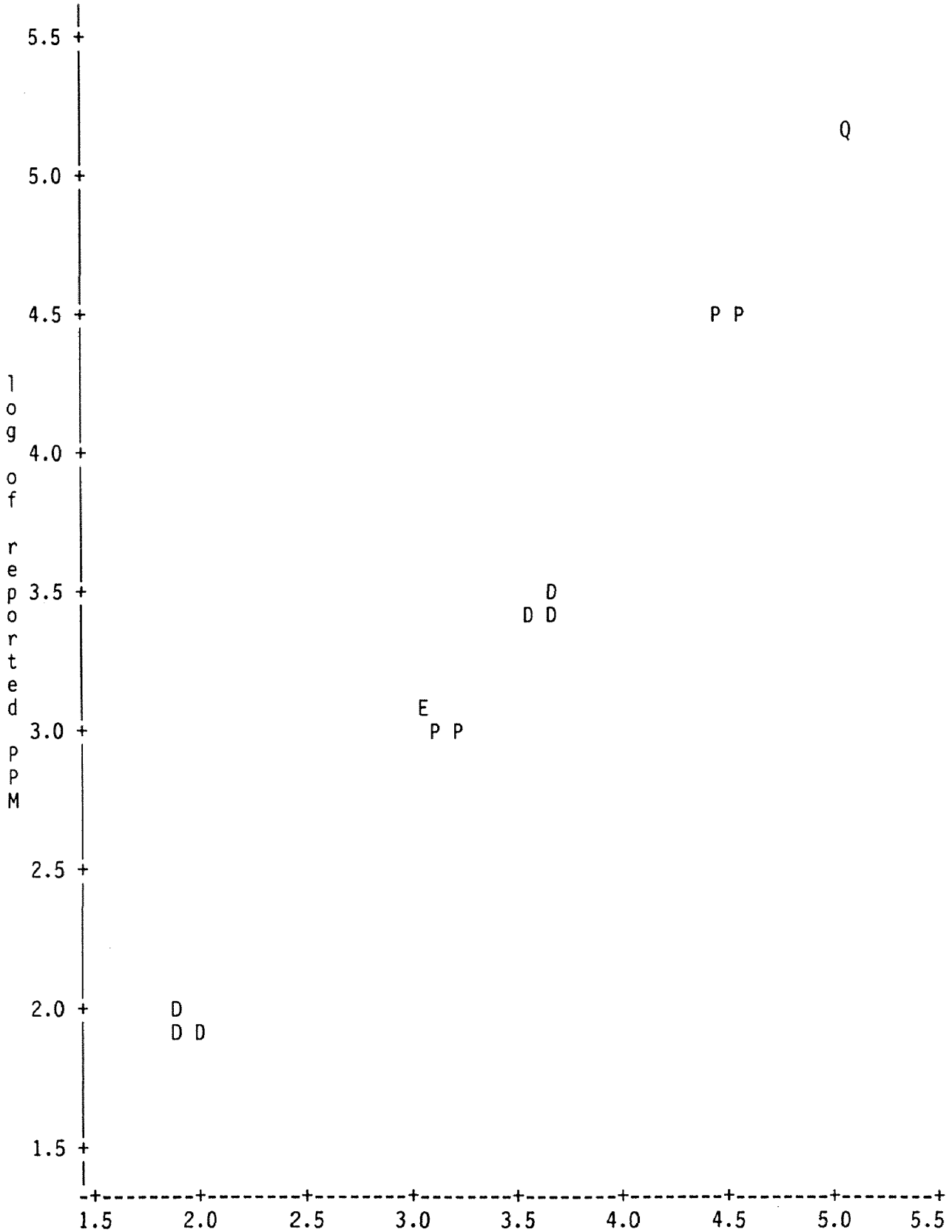
Plot of REC*LOGTRUE. Symbol is value of MTX.



NOTE: 4 obs hidden.

---------- METH=5 LAB=56 ----------

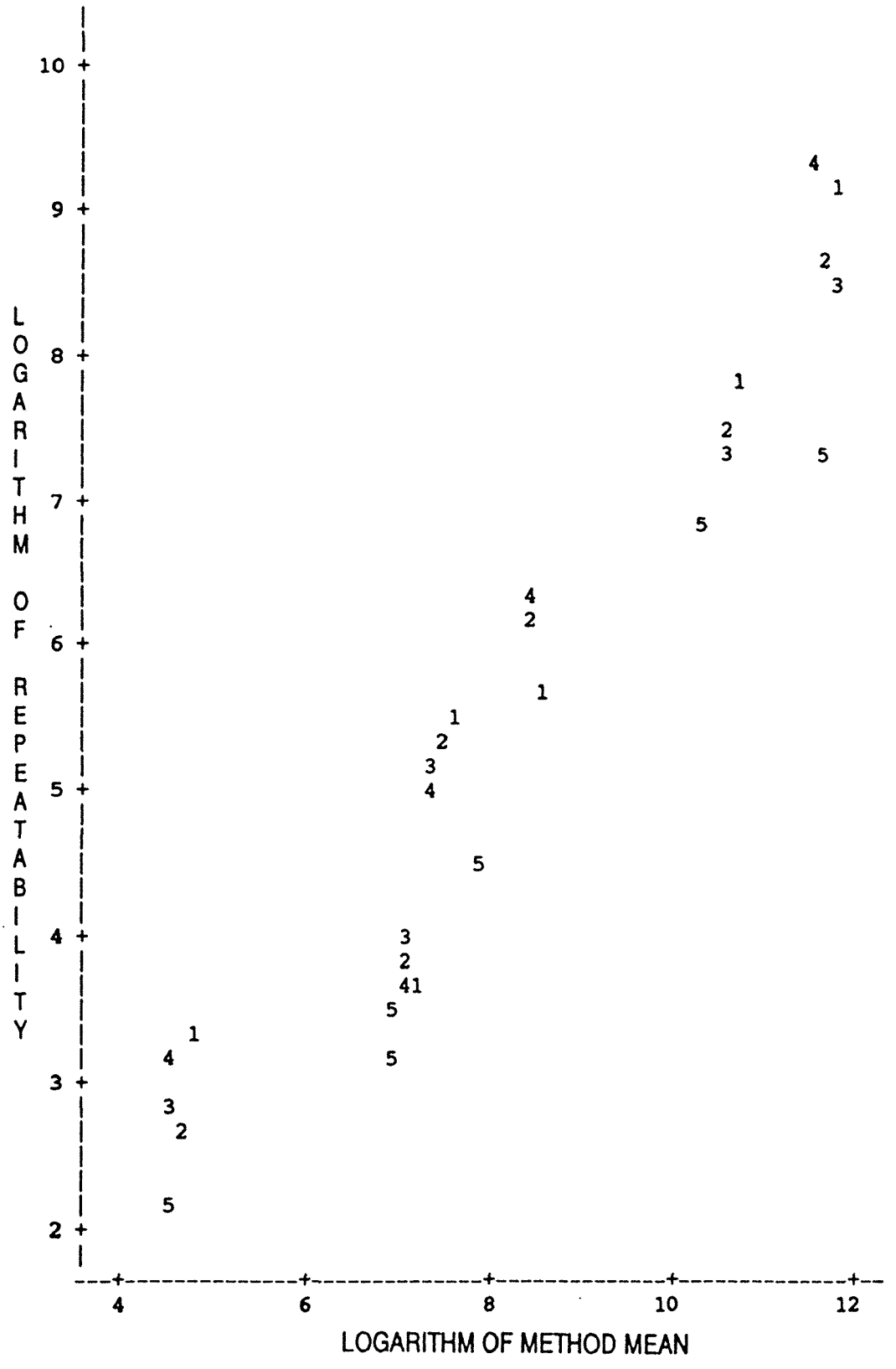
Plot of LOGCONC*LOGTRUE. Symbol is value of MTX.



NOTE: 8 obs hidden.

Appendix G-8

Plots of Repeatability/Reproducibility versus Lead Concentration



Plot of Log Repeatability versus Log Method Mean.

Legend
1 = MS/AAS
2 = HP/AAS
3 = MW/ICP
4 = HP/ICP
5 = Lab XRF

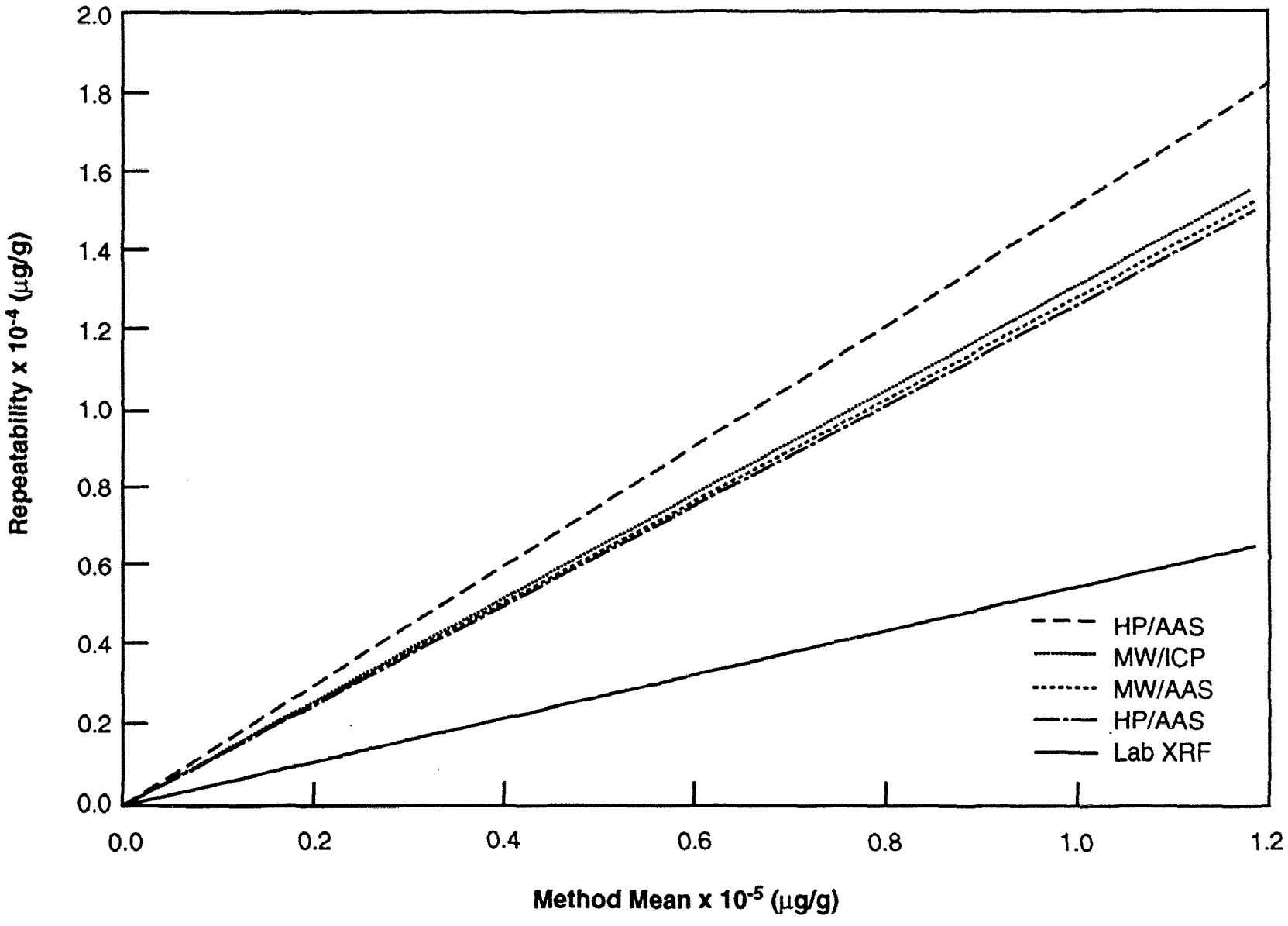
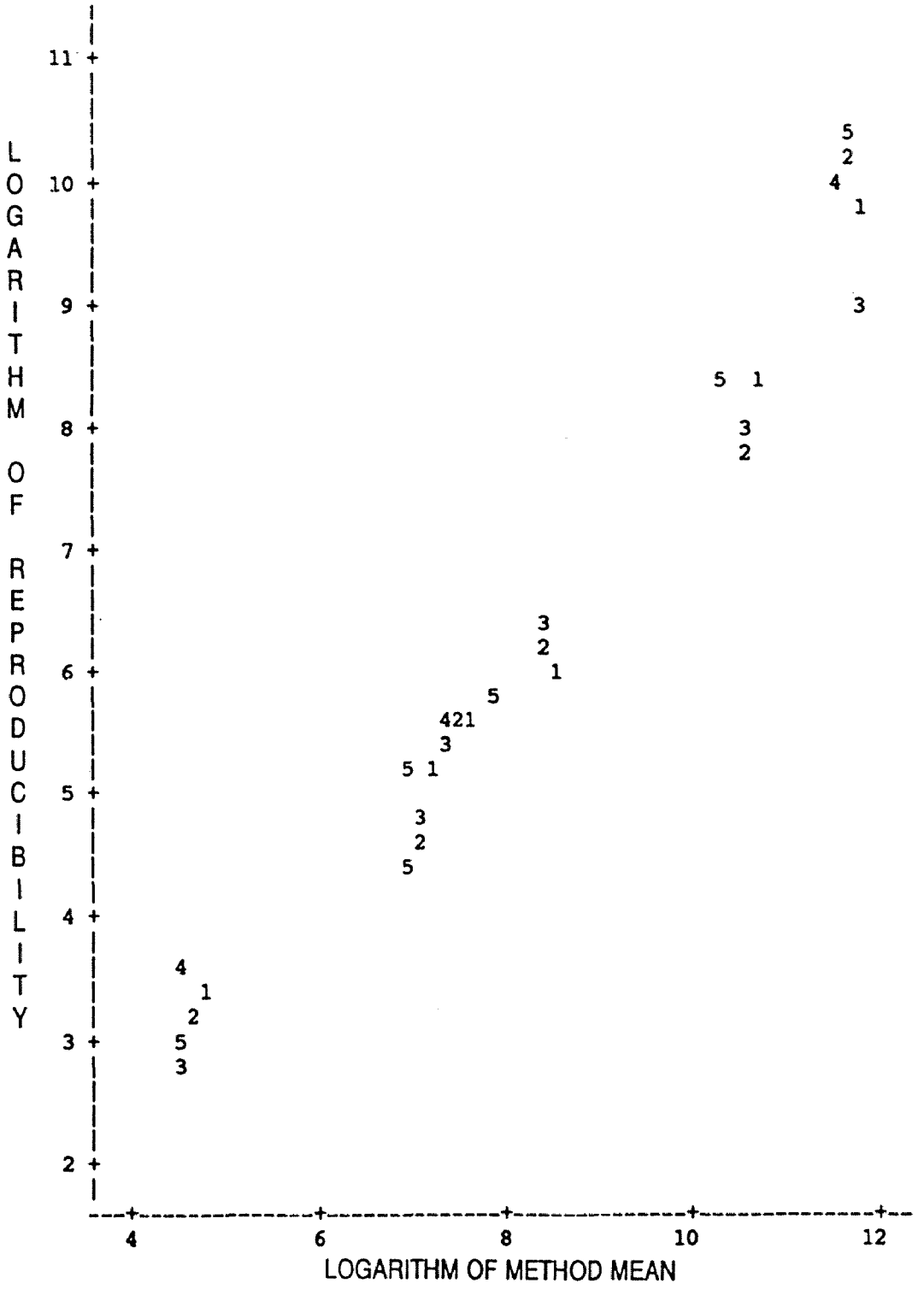


Figure 1. Repeatability versus lead concentration by method.



Plot of log of Reproducibility versus log of Method Mean (µg/g).

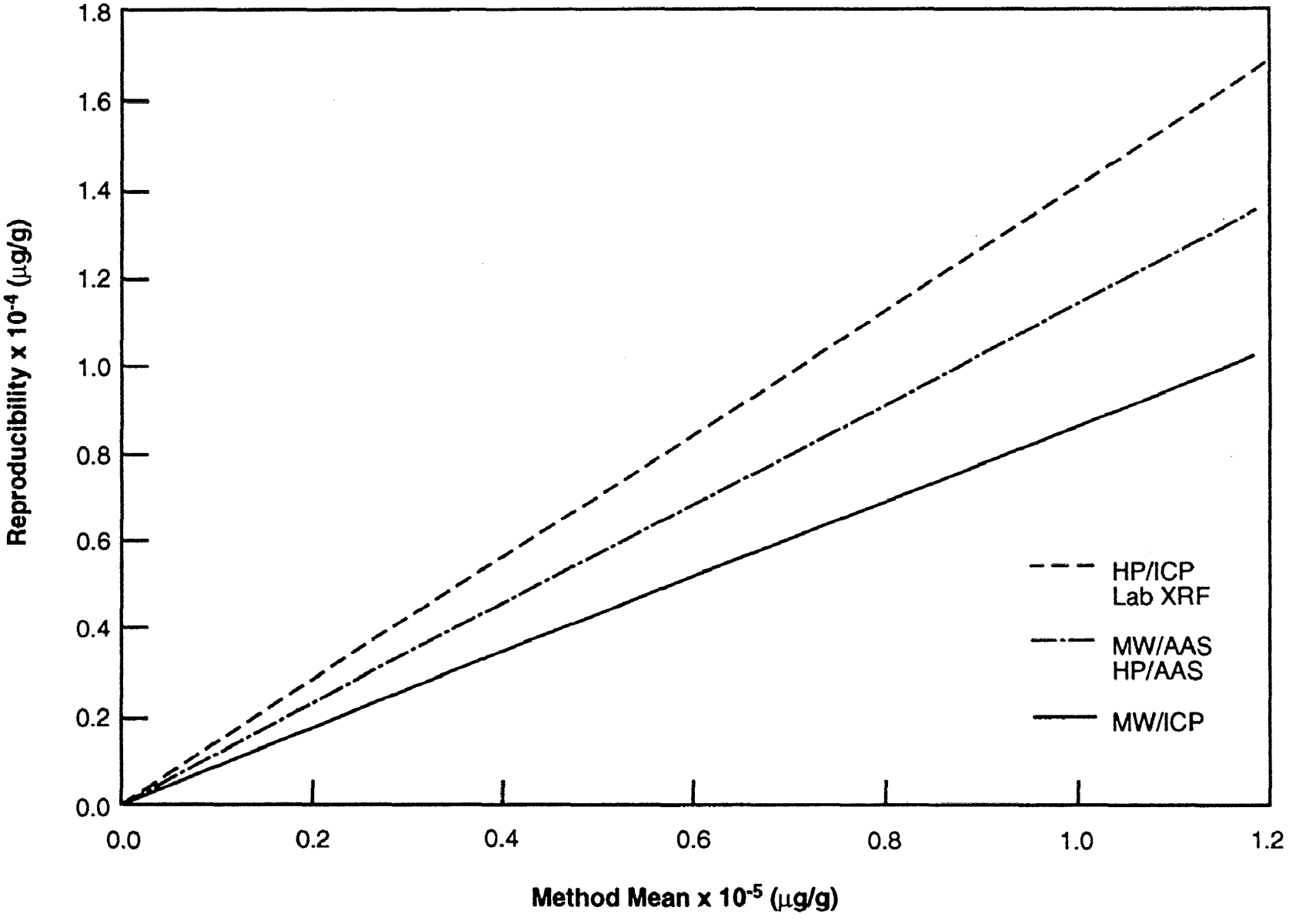
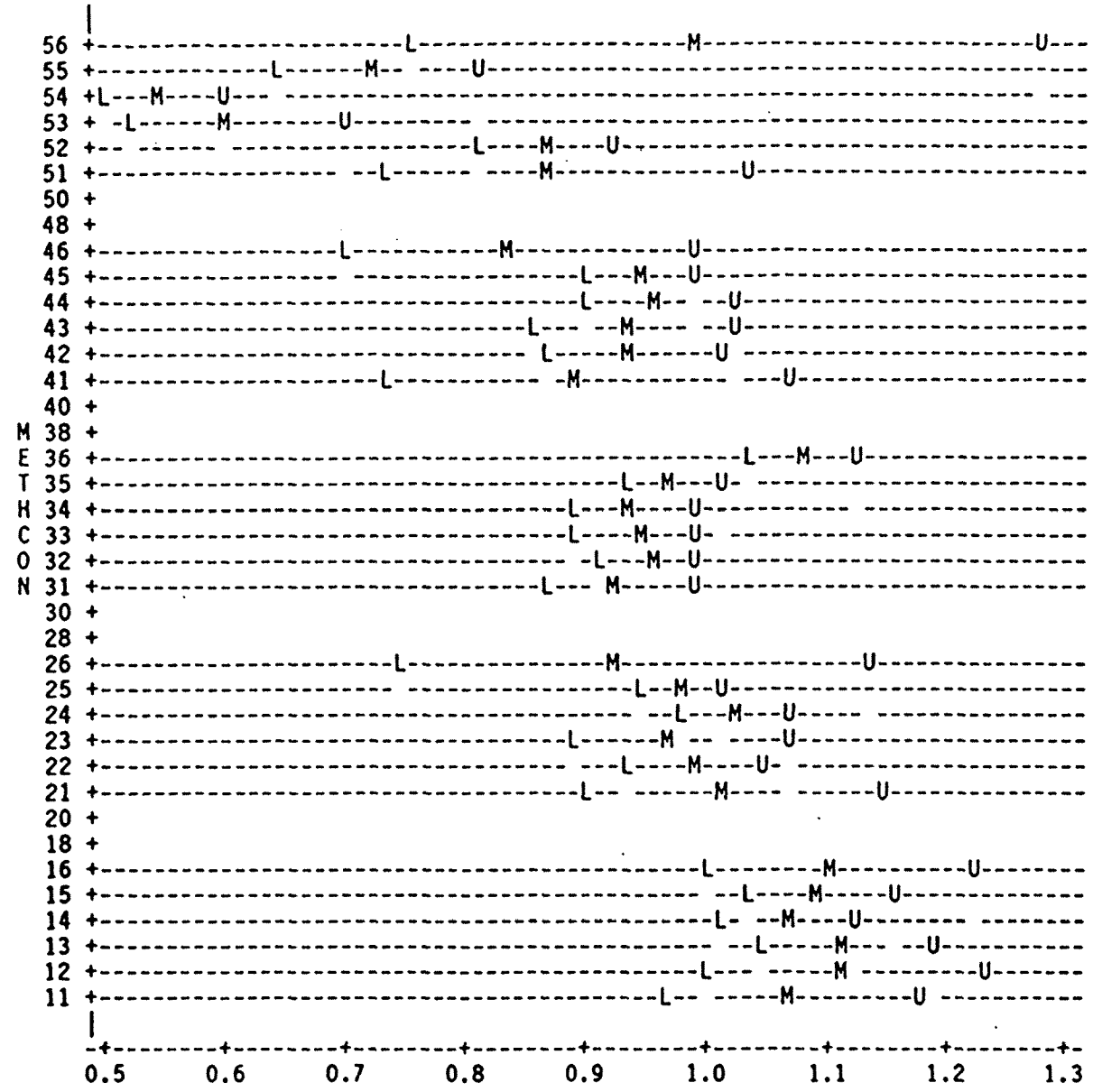


Figure 2. Reproducibility versus lead concentration by method.

Appendix G-9

Geometric Mean Recovery by Method



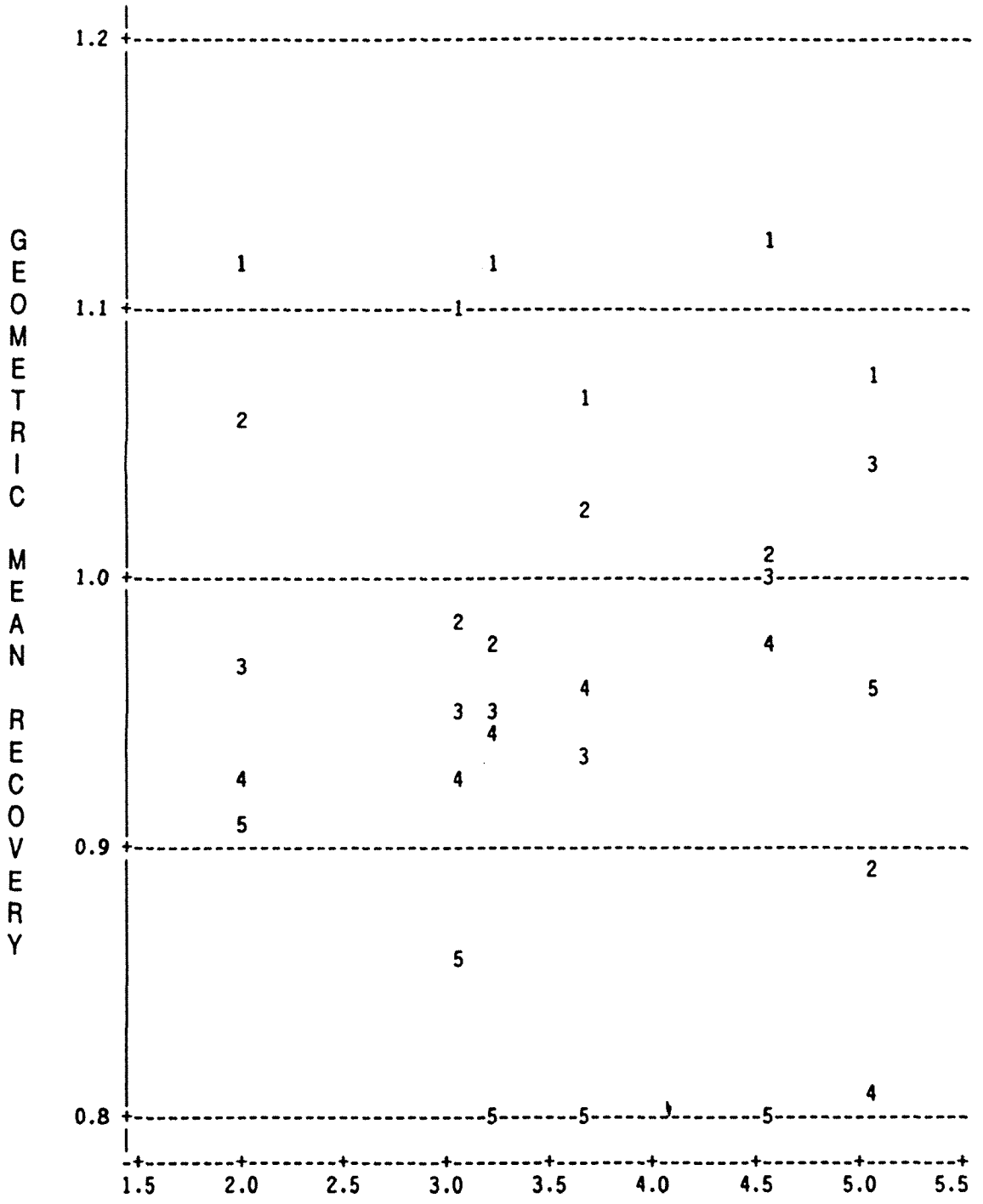
95% Confidence Intervals for Geometric Mean Recovery
for Each Method and Sample.

LEGEND

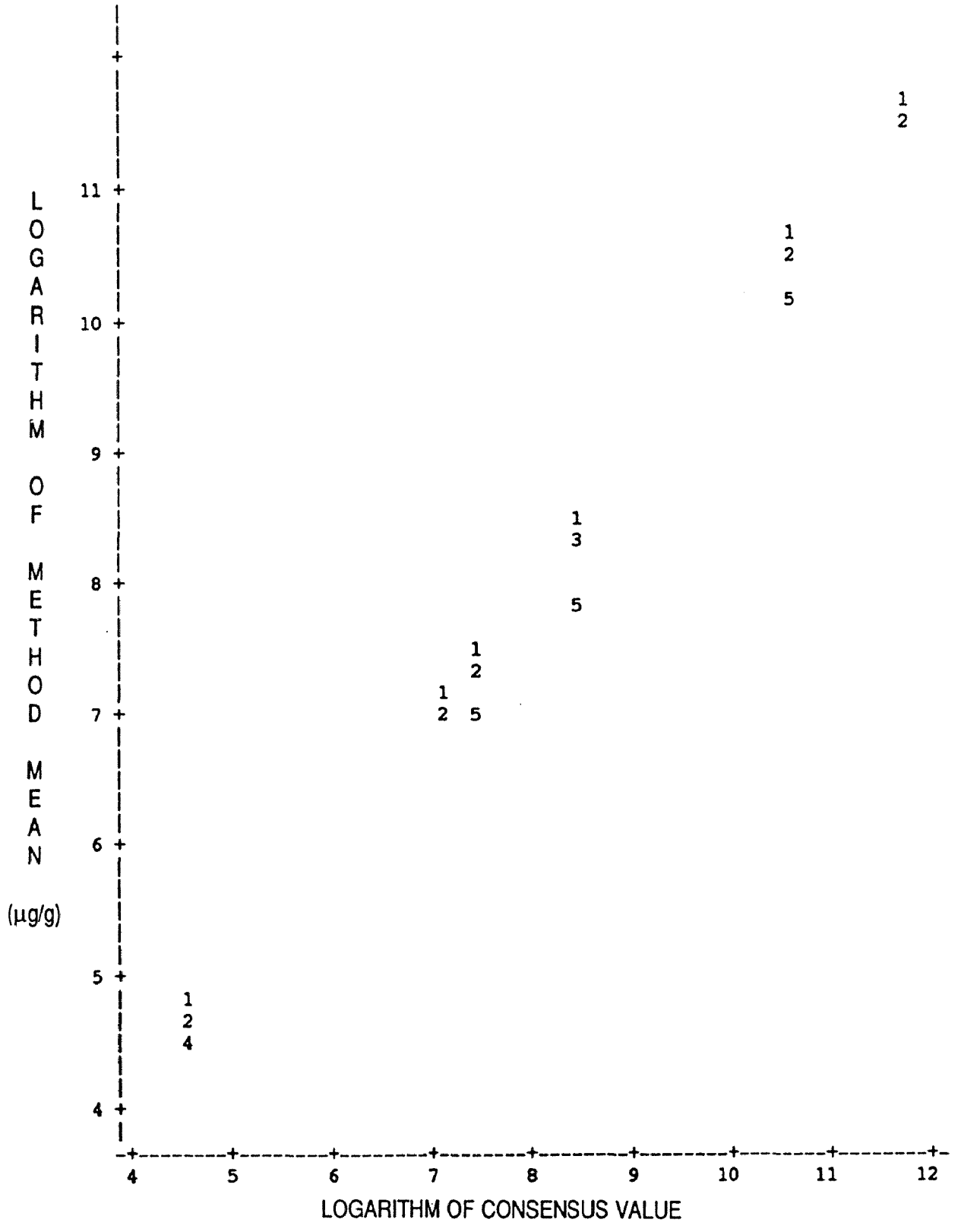
95% Confidence Interval for Geometric Mean Recovery
L = Lower Limit
M = Mean
U = Upper Limit

METHCON
The first digit denotes method number
1 = MW/AAS
2 = HP/AAS
3 = MW/ICP
4 = HP/ICP
5 = Laboratory XRF

The second digit denotes rank of concentration for sample
1 = Low Dust
2 = Dust SRM
3 = Low Paint
4 = High Dust
5 = High Paint
6 = Paint SRM



Demonstration of method effect via geometric mean recovery versus log consensus value (Method 5 censored at .8).



Log of Method Mean versus Consensus Value.

Legend
1 = MS/AAS
2 = HP/AAS
3 = MW/ICP
4 = HP/ICP
5 = Lab XRF

Appendix G-10

Method Effects and Pairwise Comparison of Method Means

Tests for method effects and pairwise comparison of method means.

The overall F-tests for significance of method effects were not significant for the low dust sample ($p = .44$), were only marginally significant for the paint SRM ($p = .08$), but were highly significant on the other four samples ($p < .001$ in all cases).

For pairwise comparisons of method means within each of the six samples, ordinary nonsimultaneous t-tests at the 5% significance level were used. There are ten possible paired comparisons of methods within each of the six samples, so that three false rejections of the hypothesis of no difference would be expected by chance alone.

The results of the pairwise comparisons are summarized below. No differences were declared in connections with the low dust sample, and only two differences were declared on the paint SRM samples. It is clear from the table below that the differences primarily involve methods 1 and 5. Of 28 declared differences, 26 involve methods 1 and 5. These results confirm those obtained by the simple nonparametric logic, namely, method 1 is generally higher and method 5 is generally lower than the other methods. There are, of course, exceptions, notably the low dust sample.

Results of sample-specific pairwise method comparisons.

M	E	T	H	O	D
	1	2	3	4	
2	CDE	XXXXXXXXXXXXXXXXXXX XXXXXXXXXXXXXXXXX			
3	ACDE	A	XXXXXXXXXXX XXXXXXX		
4	ACDEF	None	F	XXX	
5	ACDE	ACDE	ADE	ADE	

Table entries indicate samples for which method comparisons are significantly different using ordinary nonsimultaneous t-tests at the 5% significance level. For instance, methods 3 and 5 were declared different on samples A, D, E.

Legend
A = High Dust
B = Low Dust
C = Dust SRM
D = High Paint
E = Low Paint
F = Paint SRM

Tests for method effects

Several other effects are suggested. In addition to the facts that MW/AAS is uniformly higher and XRF uniformly lower than the other methods, there appear to be other effects due to analytic method or extraction method, as indicated by the results of comparisons using the SAS General Linear Model procedure. These comparisons were limited to non-XRF methods. Low p-values indicate significant effects.

Tests for effect of method of analysis, by matrix and method of extraction

Extraction	Matrix	p-value
MW	dust	<.01
MW	paint	<.01
HP	dust	.06
HP	paint	.36

Tests for effect of method of extraction by matrix and method of analysis

Analysis	Matrix	p-value
AAS	dust	.02
AAS	paint	<.01
ICP	dust	.92
ICP	paint	.03

Appendix H

Total Microwave Digestion Method

RTI Method for Total Digestion of Lead in Paint and Dust

Procedure 1: U. S. Fish and Wildlife Service Digestion

- Weigh 100 mg of ground paint into a clean Teflon digestion vessel.
- Add 5 mL of conc. HNO_3 and 1 mL of 49% HF.
- Cap the vessel and microwave at the following conditions:
  - 3 min at 255 power,
  - 3 min at 50% power,
  - 3 min at 100% power.
- Allow solution to cool to room temperature; uncap Teflon digestion vessel.
- Evaporate residue to a volume of 2 - 3 mL.

Procedure 2: Institute of Chemical Industry and Metallurgy of China Digestion

Prepare 12 digestates as follows:

- Transfer contents from Procedure 1 into a 120 mL Teflon PFA vessel, rinsing walls of vessel with DI water.
- Add 10 mL conc. HCl and 0.5 mL HF.
- Microwave at the following conditions for ICP analysis:
  - 10 minutes at 80% power,
  - 8 minutes at 60% power, or

  Microwave at the following conditions for AAS analysis:
  - 10 minutes at 80 % power,
  - 5 minutes at 60% power.
- Allow solution to cool to room temperature; uncapTeflon digestion vessel.
- Add 6 mL of 4% boric acid, and 15 ml of conc. HCl.
- Transfer to 100 mL volumetric flask and dilute to volume.

U.S. Fish and Wildlife Service Procedure

DIGESTION OF ANIMAL TISSUE

Method 201 - ICP
Digestion of Animal Tissue

Metals of Reference: Al, Sb, Ba, Be, B, Cd, Co, Cr, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Ag, Sr, Sn, V, Zn

1.0 Reagents

1. Concentrated nitric acid - instra-analyzed
2. Source of laboratory pure water; Type II, etc.

1.1. Materials and Apparatus

1. CEM MDS-81D microwave oven
2. Top loader analytical balance accurate to 0.001 grams
3. 120 mL digestion vessels - PFA Teflon
4. 50 mL polypropylene volumetric flasks
5. 60 mL polypropylene sample bottles
6. Disposable polypropylene funnels - 55 mm

1.2 Method

1. Weigh out 0.5 grams freeze-dried, homogenized material accurately to 0.001 grams into a clean 120 mL microwave digestion vessel.

2. Add 5 mL Baker Instra-Analyzed concentrated nitric acid.

3. Place cap on vessels and torque to 12 ft-lbs using CEM capping station or torque wrench.

4. Place vessels onto turntable and load into CEM MDS-81D microwave oven.

5. Heat the vessels:

   a) 3 minutes at 20% power
   b) 3 minutes at 50% power
   c) 15 minutes at 75% power

6. Upon completion of heating cycle, wait 1 minute, then remove vessels from oven and cool in a fume hood.

7. When cool, uncap vessels using capping station and carefully evaporate vessel contents to 0.5 - 1.0 mL residue and dilute to 10 mL with deionized water.

Determination of Si, Al, Ca, Mg, Fe, Ti, Mn, Cu, Ci and Ni In Vanadium - Titanium - Iron Ore by Microwave Oven Digestion, ICP, AA and Chemical Analysis Methods

Li Bao-hou
Yu Zhong-quan
Han Kai

Institute of Chemical Industry and Metallurgy
The Academy of Sciences of China

June 1988
Beijing, China

Institute of Chemical Industry and Metallurgy

Acid Digestion of Samples by Microwave Oven

1. Standard Samples of Pan Zhi Hua, Academy of Iron and Steel, Ministry of Metallurgy, China

   BH 0102 vanadium - titanium fine ore

   BH 0104 titanium fine ore

2. Microwave Oven Equipment:

   Model MDS - 81D Microwave Oven (product of CEM, U.S.A.) with capping station, cooling groove and 120 mL Teflon PFA vessel

   Settings of MDS - 81D operation program:

	ICP ANALYSIS		AA ANALYSIS	
	Time	Power	Time	Power
Program 1:	10 minutes	80%	10 minutes	80%
Program 2:	8 minutes	60%	5 minutes	60%

3. Methods of Sample Dissolution:

Put 0.1 gram accurately weighed standard sample (BH 0102) into a 120 mL Teflon PFA vessel, rinse the wall of the vessel with small quantity of deionized water and add 10 mL concentrated hydrochloric acid and 0.5 mL hydrofluoric acid. Secure the safety valve on the vessel and tighten the vessel cap on the capping station. Place the vessel on the carousel and connect the exhaust tubes. The operation for the BH0104 standard sample is the same as above except 10 mL concentrated acid and 2 mL hydrofluoric acid are added.