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CAPILLARY COLUMN GC-MS DETERMINATION OF 77 PURGEABLE ORGANIC COMPOUNDS IN TWO SIMULATED LIQUID WASTES

by

M. F. Yancey, R. A. Kornfeld, and J. S. Warner
BATTELLE
Columbus Division
Columbus, Ohio 43201-2693

Project Officer

Thomas Pressley
Physical and Chemical Methods Branch
Environmental Monitoring and Support Laboratory

Environmental Monitoring and Support Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

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For each of the remaining 77 compounds, the linear concentration range and detection limit were determined with data obtained by PTD GC-MS analysis of spiked reagent water. A relative standard deviation (RSD) of ≤25% for the average response factor was chosen as the acceptance criterion for determining the linear range. This criterion was met over a concentration range of at least two orders of magnitude for 56 of the 77 analytes, 1.5 orders of magnitude for 12 analytes, and 1 order of magnitude for 6 analytes. The criterion was not met for acetone, trichlorofluoromethane, and 2-chloro-1,3-butadiene.

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NOTICE

FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, Ohio, conducts research to:

o   Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.

o   Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microbiological organisms in water, and to determine the responses of aquatic organisms to water quality.

o   Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

This report presents results obtained when capillary column gas chromatography-mass spectrometry was used to determine applicable concentrations ranges for 77 purgeable organic compounds and to assess the accuracy and precision of measurements of those compounds spiked into two simulated liquid wastes, a municipal sludge leachate and reagent water containing fulvic acid.

Thomas A. Clark, Acting Director
Environmental Monitoring and Support
Laboratory - Cincinnati

ABSTRACT

The suitability of purge-trap-desorb (PTD) procedures for determination of 84 volatile organic compounds with capillary column gas chromatography (GC) and mass spectrometry (MS) was evaluated. After collecting GC-MS data not previously available for some analytes, 7 of the 84 compounds were eliminated from further consideration because of poor purging efficiency or analyte instability.

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Method performance was assessed by analyzing eight replicate aliquots of two simulated liquid waste samples (a municipal sewage sludge leachate and water containing fulvic acid) containing analytes spiked at two concentrations. For >80% of the analytes, bias of measured concentrations was $\leq 30\%$. For most other analytes bias was $>+30\%$. The observed high positive bias was attributed to enhanced sensitivity caused by high concentrations of ions in the MS source. Calibration data showed that short-term (daily) and long-term (two weeks) precision was very good.

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SECTION 1

INTRODUCTION

In Appendix IX to 40 CFR Parts 264 and 270, the Resource Conservation and Recovery Act specifies over 200 organic compounds used to screen for suspected groundwater contamination at land-based hazardous waste treatment, storage, and disposal facilities (FR, 52, July 9, 1987, pp. 25942-25953). Analytical methods for most of these analytes are included in "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods" (SW-846, Third Edition, November 1986).

The SW-846 method recommended for determining volatile, relatively water insoluble organic analytes is Method 8240, which uses purge-trap-desorb (PTD) analyte extraction followed by packed column gas chromatographic (GC) separation and mass spectrometric (MS) detection and measurement. Advances in GC column technology now permit detection and quantitation of a wider range of compounds in a shorter time with greater sensitivity using a fused silica or glass capillary column. For example, USEPA Method 524.2 uses a 0.75 mm i.d. glass capillary column for GC-MS determinations of volatile organic compounds in drinking waters.

As part of an ongoing effort to demonstrate the applicability of present USEPA analysis methods and/or to develop new methods, the suitability of room temperature PTD coupled with capillary column GC-MS determinations of volatile organic compounds was evaluated. Of the 84 compounds included in this study, data were obtained for 77 compounds to establish the applicable concentration range for each analyte. The method was also evaluated for accuracy and precision of measurements of analytes added to two simulated liquid wastes, a water containing fulvic acid and a publicly owned treatment works (POTW) sewage sludge leachate.

SECTION 2
CONCLUSIONS

The following conclusions are based on the experimental results of this project:

o The use of methanol as a solvent interferes with the chromatographic performance of a nonpolar capillary column for the determination of polar volatile compounds such as acetonitrile, isobutyl alcohol, and propargyl alcohol.

o Hexachlorocyclopentadiene, 2-chloroethyl vinyl ether, and pentachloroethane are not very stable in methanol.

o 1,4-Dioxane is not sufficiently purged from water at room temperature to be determined by a PTD procedure.

o Methanol and water desorbed from a trap containing Tenax, silica gel, and charcoal, interfere with the chromatographic performance of a nonpolar capillary column for the determination of gaseous and very low boiling nonpolar compounds by a PTD procedure.

o A total of 74 of the 84 volatile compounds studied can be determined satisfactorily by SW-846 Method 8240 using a VOCOL capillary column.

o 2-Chloro-1,3-butadiene is lost by polymerization during the trap desorb process; the degree of polymerization and, therefore, the percent loss, increases as the concentration increases.

o With MS conditions that permit Method 8240 performance criteria to be met using a capillary column and 250 ng of internal standard, an increased sensitivity may result from high ion concentrations in the MS source.

o A calculated MDL was often considerably lower than the lowest concentration at which an analyte was detected experimentally.

SECTION 3
RECOMMENDATIONS

The following recommendations are made based on the results from method range and matrix validation studies:

o Of the 77 compounds for which method performance data were obtained, 74 (all but acetone, trichlorofluoromethane, and 2-chloro-1,3-butadiene) should be appropriate analytes for a capillary column version of Method 8240. Acetone may be suitable if a different quantitation ion (i.e., m/e 58) is selected.

o Evaluate changes in GC-MS system operating conditions to allow the electron multiplier to become saturated at lower analyte concentrations if lower detection limits are required.

o Investigate cryofocusing or other means to focus early eluting compounds to minimize peak broadening and improve quantitation, especially at low concentrations.

o Use a non-volatile, water soluble solvent for spiking solutions to avoid deleterious chromatographic effects caused by methanol and to improve performance of early eluting analytes.

o Investigate differences between calculated and observed MDLs to establish a protocol for obtaining more meaningful MDLs.

o Evaluate the effect of MS ion source tuning and cleanliness on changes of analyte response factors with concentration.

SECTION 4
EXPERIMENTAL

ANALYTES

A total of 84 organic compounds were considered for inclusion in this study. The 84 compounds include all Method 524.2 analytes and all Appendix IX compounds that might reasonably be expected to be determined by room temperature PTD extraction followed by GC-MS analysis using a 0.75 mm i.d. glass capillary column.

Of the 84 analytes, 21 were obtained as individual methanol solutions (5,000-10,000 μg/mL) from the USEPA Repository for Toxic and Hazardous Materials, 28 were purchased as four mixtures in methanol, 34 were purchased individually in neat form, and 1 (2-chloro-1,3-butadiene) was purchased as a 50% xylene solution.

PTD-GC-MS ANALYSES

Analyses were conducted in accordance with Method 8240 procedures. Equipment included a Tekmar Model LSC-2 PTD system, a Carlo Erba Model 4160 GC, a Finnigan Model 3200 MS fitted with a glass jet separator, and an Incos data system with Revision 5.5 software. The PTD system was fitted with a 5-mL fritted glass purge tube and a 305 mm x 4 mm i.d. stainless steel trap containing 10 mm of 3% SP-2100 on Supelcoport, 77 mm of Tenax, 77 mm of silica-gel, and 77 mm of coconut charcoal. The system was operated with helium purge for 11 min at 26 mL/min at room temperature (23-25°C), desorption for 4 min at 15 mL/min at 180°C, and trap bake for 7 min at 26 mL/min at 180°C. The GC was fitted with a 60 m x 0.75 mm I.D. Supelco VOCOL column coated with a 1.5 μm film and operated with a helium carrier gas flow of 15 mL/min. The column temperature was maintained at 10°C during the desorb cycle, programmed to 200°C at 10°C/min at the end of the desorb cycle, and maintained at 200°C for 10 min. The MS was tuned daily to meet bromofluorobenzene criteria and was operated with an emission current of 0.27-0.37 ma, an electron multiplier voltage of 1200-1800 V, and a scan time of 1 sec over a mass range of 35-325 amu. The emission current was selected to achieve acceptable tuning and to stay within the range recommended by the manufacturer. The electron multiplier voltage was

set slightly lower than a setting that would cause saturation for any analyte at 200 µg/L (2000 µg/L for 15 poorly purged analytes). This setting permitted analytes to be detected without multiplier saturation at concentrations up to four times the internal standard (IS) concentration of 50 µg/L specified by Method 8240, and allowed maximum dynamic range.

The system met all daily performance criteria specified by Method 8240. In addition to BFB tuning criteria, these criteria include (1) minimum response factor (RF) of 0.30 for each of the five system performance check compounds (chlorobenzene, chloromethane, 1,1-dichloroethane, 1,1,2,2-tetrachloroethane, and tribromomethane); (2) RF difference of $\leq 25\%$ for the six calibration check compounds (chloroform, 1,1-dichloroethene, 1,2-dichloropropane, ethylbenzene, toluene, and vinyl chloride); (3) IS retention time variation of ≤ 30 sec, and (4) IS area variation of $\leq 50\%$.

PREPARATION OF STOCK SOLUTIONS

Stock methanol solutions of each of the 34 compounds obtained in neat form were prepared with procedures described in Method 8240 and stored at -10°C. Those solutions, the 21 solutions supplied by USEPA, and the five commercial solutions were used to prepare four mixed stock solutions. All analytes in a given mixed stock solution were present at the same concentration. The amounts of 1,2-dimethylbenzene and 1,4-dimethylbenzene added from their respective stock solutions were decreased by the amounts (determined by GC analysis with flame ionization detection) contributed by xylene solvent—for the stock solution of 2-chloro-1,3-butadiene. One of the mixed stock solutions (Mix 1) contained only the most water-soluble analytes that were known to have low purging efficiencies. Another one of the mixed stock solutions (Mix 2) was devoted to analytes expected to give apparent low purging efficiencies primarily because of hydrolytic or thermal stability problems.

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PRELIMINARY STUDIES

The four mixed stock solutions prepared from individual stock solutions and the four commercial solutions containing mixtures of analytes were analyzed by direct injection to determine GC performance and obtain mass spectra for all analytes under the GC-MS conditions described previously.

Two of the mixed stock solutions, Mix 1 and Mix 2, were analyzed at concentrations of 200 µg/L and 2,000 µg/L in reagent water to obtain purging efficiencies. Purging efficiencies were determined by comparing analyte/IS area ratios from PTD analyses of water spiked with 1 µg or 10 µg of analyte with those obtained by direct injection of 1 µg of analyte. Seven analytes that were not detected by direct injection or had purging efficiencies of <5% were eliminated from further consideration. Fresh solutions of Mix 1 and Mix 2, in which these compounds were deleted, were prepared for all subsequent studies. These two mixes contained the 15 compounds that were most water-soluble and expected to give low apparent purging efficiencies but had passed the preliminary tests. Those 15 compounds, henceforth referred to as the poorly purged analytes, were:

o Acetone   o Hexachloropropene

o Acrolein   o 2-Hexanone

o Acrylonitrile   o Methacrylonitrile

o Bis-(2-chloroethyl) ether   o Methyl methacrylate

o 2-Butanone   — o 4-Methyl-2-pentanone

o 2-Chloroethyl ethyl ether   o Propionitrile

o trans-1,4-Dichloro-2-butene   o Vinyl acetate

o Ethyl methacrylate.

PREPARATION OF SPIKING SOLUTIONS

Stock solutions were combined into a high-concentration spiking solution that contained the 15 poorly purged analytes at a concentration of 100 µg/mL and all other analytes at 10 µg/mL. That solution was diluted to obtain a low-concentration spiking solution containing the poorly purged analytes at a concentration of 3 µg/mL and all other analytes at 0.3 µg/mL. The two spiking solutions were stored at -10°C until needed.

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METHOD RANGE STUDIES

For the method range studies, the low-concentration and high-concentration spiking solutions were used to spike 5-mL aliquots of reagent water to obtain 13 concentrations ranging from 1 to 5500 μg/L for the poorly purged analytes and 0.1 to 550 μg/L for all other analytes. The low concentration spiking solution was used to obtain spike concentrations of 1 to 55 μg/L for the poorly purged analytes and 0.1 to 5.5 μg/L for all other analytes. The high concentration spiking solution was used to obtain all higher analyte concentrations. Eight replicate samples were analyzed for each of the 13 spike concentrations.

Acquired data were analyzed by a semiautomated process to minimize analyst effort. A project-specific mass spectral library was generated containing the retention time and quantitation ion of each analyte and IS. The quantitation ion was chosen for maximum sensitivity while attempting to avoid interferences from coeluting materials. For the majority of analytes, the quantitation ion selected was the base peak. For those analytes listed in Method 8240, the primary ion specified in Method 8240 was used as the quantitation ion.

A reverse library search of the data was performed by the MS data system. For each analyte for which the quantitation ion was detected above the background, an RF was calculated using the equation:

$$RF = (A_a \times C_{IS})/(A_{IS} \times C_a),$$

where

A_a = peak area of analyte

A_{IS} = peak area of internal standard

C_a = concentration of analyte

C_{IS} = concentration of internal standard.

An estimated detection limit (EDL) for each analyte was determined by a trained analyst's manual inspection of the mass spectrum from one of the replicate samples at the lowest concentration for which the computer detected the quantitation ion in at least four replicates. The analyst determined the presence of the analyte by examining the extracted ion current profiles of 2-5 major ions, including the quantitation ion, selected from the reference mass spectrum. The analyte was considered to be present if the major ions maximized simultaneously and had relative intensities within 20% of those in the reference mass spectrum, as specified in Method 8240, and if the quantitation

ion gave an area response greater than 1000 or a signal-to-noise ratio of at least three to one. If, in the analyst's opinion based on the above criteria, the mass spectrum confirmed the presence of the analyte in question, that concentration was considered to be the EDL. If, in the opinion of the analyst, the mass spectrum did not confirm the presence of the analyte, the manual inspection process was repeated at the next higher concentration.

Mean RFs and RSDs of measured RFs were calculated at each concentration as the first step in determining the linear concentration range for each analyte (Table 2). High concentration results were evaluated for system saturation by plotting and visually evaluating the RF as a function of analyte concentration. If an RF decreased with increasing concentration, the high concentration was eliminated from the linear range. An average RF and RSD of retained RFs were computed using RFs from all concentrations other than high concentrations rejected as described above. If the RSD was >25% (an acceptance threshold selected with USEPA personnel concurrence), the concentration range was narrowed in an attempt to reduce the RSD ≤25%, but the concentration range was never decreased below one order of magnitude.

The lowest concentration at which the analyte was found and quantified in at least four of eight replicates was considered to be the EDL, regardless of the RSD of measured RFs. For each analyte, data obtained at the EDL were used to calculate a method detection limit (MDL) using the USEPA procedure described in Appendix B to 40 CFR Part 136 (Federal Register 49, 198, October 26, 1984).

MATRIX VALIDATION STUDIES

Two simulated liquid waste samples were spiked and analyzed to evaluate method accuracy and precision. One sample was a municipal sewage sludge leachate prepared using a modification of the USEPA toxicity characteristic leaching procedure (Federal Register, 51, 21685, June 13, 1986). The modification included using a smaller sample and shorter extraction time than specified. Centrifuge bottles (250 mL) were filled with a mixture of sludge and 1 M, pH 5 acetate buffer extraction fluid (20 mL of extraction fluid per gram of solids in the sludge) with zero headspace. After glass beads were added to facilitate mixing, bottles were tumbled end-over-end for 2 h. The mixture was centrifuged and filtered, using care to minimize loss of volatile components. The other sample was an artificial ground water prepared by adding

fulvic acid (Suwannee Stream Reference, U.S. Geological Survey, International Humic Substance Society) to reagent water at a concentration of 1 mg/L. The prepared samples were stored as aliquots in 40-mL septum-capped vials with zero headspace in a refrigerator until used for analysis.

For each of the two samples, eight unspiked replicates and eight replicates of each of two sets of spiked samples were analyzed. Each aliquot of one set of spiked samples contained 20 μg/L of most analytes but 200 μg/L of the poorly purged analytes. The other set contained 200 μg/L of most analytes but 2000 μg/L of the poorly purged analytes. Calibration standards prepared by spiking reagent water with the each analyte at a concentration of 50 μg/L or 500 μg/L for the poorly purged analytes were analyzed at the beginning, middle, and end of each day. Spiked samples and reagent water were analyzed immediately after spiking.

For each analyte, a daily mean RF was calculated from data obtained by analyses of three calibration solutions. Analyte concentrations measured (C_m) in the spiked samples were calculated using the equation:

$$C_m = (A_a \times C_{IS})/(A_{IS} \times RF),$$

where

RF = daily mean response factor from analysis of three calibration solutions.

The accuracy (A) of each mean measured concentration was calculated using the equation:

$$\% A = [(C_m - C_0)/C_s] \times 100,$$

where

        C_0 = concentration of analyte in unspiked matrix

        C_s = concentration of analyte spiked into the matrix.

Each calculated accuracy was therefore corrected when an analyte was found in an unspiked sample. An average accuracy and RSD of measured concentrations was calculated for each analyte at each spiking concentration in each matrix.

SECTION 5
RESULTS AND DISCUSSION

PRELIMINARY STUDIES

Six analytes (acetonitrile, isobutyl alcohol, and propargyl alcohol, hexachlorocyclopentadiene, 2-chloroethyl vinyl ether, and pentachloroethane) were not detected by direct injection of 1 µg and were eliminated from further consideration. Also eliminated was 1,4-Dioxane, which had a very poor purging efficiency, 0.5% at 2000 µg/L. The methanol injection solvent probably interfered with determination of the highly polar compounds (acetonitrile, isobutyl alcohol, and propargyl alcohol) by spreading them into a wide GC band. Hexachlorocyclopentadiene, 2-chloroethyl vinyl ether, and pentachloroethane may have decomposed during storage of the methanol spiking solution. Retention times were determined and quantitation ions were selected from the GC-MS data for all remaining 77 analytes (Table 1).

METHOD RANGE STUDIES

Because none of the 77 analytes was detected at spiking concentrations of 0.3 and 0.1 µg/L, RFs for these concentrations are not included in Table 2, which summarizes RF data for the linear range for each analyte. Of the 74 analytes having satisfactory method range and RF precision, 56 exhibited a linear range of at least two orders of magnitude and an additional 12 exhibited a range of at least 1.5 orders of magnitude. Of the remaining six analytes, three are highly volatile (dichlorodifluoromethane, chloromethane, and chloroethane) and two are poorly purged (trans-1,4-dichloro-2-butene and hexachloropropene). Those five compounds required range narrowing to reduce the average RSD of measured RFs to $\leq 25\%$. No explanation is apparent for the behavior of the sixth compound, isopropyltoluene.

Three compounds (acetone, 2-chloro-1,3-butadiene, and trichlorofluoromethane) did not produce $\leq 25\%$ RSD for measured RFs even with one order of magnitude concentration range. Acetone may yield more reliable data using m/z 58 rather than m/z 43 as the quantitation ion. A trend in decreasing RF with increasing concentration was evident for 2-chloro-1,3-butadiene, which polymerizes readily. The degree of polymerization, which would result in loss

of the monomer, would be expected to increase with increasing concentrations and could account for lower measured RFs at higher concentrations. Trichloro-fluoromethane was particularly sensitive to the effects of methanol and water on GC peak shape. Other early eluting compounds such as dichlorodifluoro-methane (20% RSD), chloromethane (23% RSD), and vinyl chloride (20% RSD) also produced mean RFs that were less precise than RFS for most other analytes. The range for a fourth compound, hexachloropropene (32% RSD of mean RFs) was not narrowed because the greatest deviation from the mean RF occurred within the linear range at 300 µg/L. For each of the 77 analytes, a calibration curve was prepared by plotting the analyte/IS area ratio versus concentration over the linear range (Appendix A).

The lowest concentration in the linear range, the EDL, and the calculated MDL for each analyte were determined (Table 3). For all but 10 analytes the EDL, the lowest concentration at which the analyte was detected and quantified (regardless of RSD of measured RFs) in at least four of eight replicates, was the same as the lowest concentration in the linear range. Lower EDLs could undoubtedly have been achieved for most analytes if MS tuning parameters and the electron multiplier voltage had been selected to achieve maximum sensitivity rather than to achieve a wide dynamic range and quantitation of high analyte concentrations. The calculated MDL was considerably lower than the EDL for all analytes except acetone. Comparison of the highest concentration at which each analyte was not detected in any of eight replicates (Table 3) shows that for each of 70 analytes the calculated MDL was even lower, usually by a factor of two to five, than a concentration at which the analyte was not detected experimentally. The low calculated MDLs reflect excellent precision at low concentrations and indicate that a calculated MDL may be misleading.

MATRIX VALIDATION STUDIES

The accuracies of measured concentrations of 74 analytes spiked into two samples (a POTW sludge leachate and a water containing fulvic acid) at two concentrations were calculated (Table 4). Because acetone, 2-chloro-1,3-butadiene, and trichlorofluoromethane, did not yield satisfactory method range results, data for those three compounds were discarded.

Measured concentrations were calculated with RFs measured by analysis of triplicate aliquots of reagent water spiked with each analyte at a concentration of 50 μg/L (or 500 μg/L for poorly purged analytes). This calibration concentration was within the linear range for all 74 analytes although it was near the upper limit (55 μg/L) for dichlorodifluoromethane. The high concentration matrix spike exceeded the linear range found in the method range study for nine compounds, bromobenzene, n-butylbenzene, sec-butylbenzene, tert-butylbenzene, dichlorodifluoromethane, trans-1,4-dichloro-2-butene, ethyl methacrylate, 4-methyl-2-pentanone, and n-propylbenzene. The low concentration matrix spike was outside the range for chloroethane.

The 74 analytes studied included all but 1 (2-chloroethyl vinyl ether) of the 30 compounds listed in Method 8240 Table 6, which specifies acceptance criteria when a quality control check sample is analyzed. (The exception, 2-chloroethyl vinyl ether, was among compounds not detected when directly injected.) For all but 1 of the remaining 29 compounds, Method 8240 acceptance criteria were achieved in both matrices at both high and low concentrations. The one exception was ethylbenzene at the high concentration in water containing fulvic acid, where a bias of +77% was observed but acceptable bias is +62%. A possible explanation of this and other high biases is presented below.

To evaluate the acceptability of accuracies of concentrations measured for each of the 74 analytes, ±30% bias was selected as an acceptance limit. This bias limit is much more stringent than the analyte-specific biases considered acceptable in Method 8240, which are generally ±50% or greater. With a bias limit of ±30% (70-130% accuracy), accuracies were acceptable for 61 of the 74 analytes spiked into the POTW sludge leachate at the high concentration and for 63 analytes at the low concentration. Acceptable accuracies were achieved for 50 of the 74 analytes added at the high concentration to water containing fulvic acid and for 70 analytes at the low concentration.

In nearly 90% of the cases in which the bias was outside the acceptance

range of ±30%, the bias was positive rather than negative. A likely explanation of the high positive biases, including that of ethylbenzene discussed earlier, is an increased sensitivity of the mass spectrometer source when ion concentrations are unusually high. This effect can be expected to be much more noticeable when a capillary column is used instead of a packed column, because a capillary column produces sharper peaks and higher momentary analyte concentrations than a packed column. The high positive bias was more prevalent at the high spike concentration than at the low spike concentration, especially for the water containing fulvic acid. The high spike concentration of 200 μg/L provides 1000 ng of analyte in 5 mL of sample purged. Calibration curves (Appendix A) for compounds such as chlorobenzene, isopropylbenzene, isopropyltoluene, styrene, and 1,2,4-trimethylbenzene, obtained in the method range study also provide evidence for increased sensitivity at higher concentrations. The effect was not as apparent in the method range study as in the matrix validation study, possibly because the ion source had been cleaned immediately before beginning the method range study. Decreased source cleanliness may enhance the effect.

For all but two cases in which the bias was negative and outside the acceptability range, the low spike concentration was involved, and the analyte was one of the 14 analytes spiked at a 10-fold higher concentration. For each of those analytes, the calibration standard provided 2500 ng, which could have produced a high ion concentration and high RF, which, in turn, could account for an important negative bias at the low spike concentration. Thus, an increased sensitivity resulting from high ion concentrations could account for essentially all biases, high and low. No evidence of a matrix effect was observed. Measured IS quantitation ion areas in spiked reagent water were very similar to those measured in spiked samples.

The observed effect of ion concentration on detector response was illustrated by plotting for each analyte the ratio of high concentration bias to low concentration bias versus total ion current at the high spiking concentration using data from analysis of water containing fulvic acid (Figure 1). The trend toward higher RF with increasing total ion concentration in the source indicates that mass spectrometer source parameters are not stable under conditions used for the high spike concentration experiments. This trend toward increasing RF with increasing concentration has also been observed for aromatic compounds by scientists in at least one other laboratory (Bill Loy and Frank

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Allen, USEPA, Region IV, personal communication).

During the six days of the matrix validation study, overall precision of measured RFs was good. For 61 of the 74 analytes, $\leq$15% RSD of measured RFs was achieved at the calibration concentration (Table 5). For all but 2 of the other 13 analytes, RSDs were <30%. The two exceptions were trans-1,4-dichloro-2-butene (33% RSD) and hexachloropropene (86% RSD). Both of these analytes produced quite variable results at all concentrations, probably because of thermal decomposition in the trap and transfer line.

The percent difference between the average RF obtained in the matrix validation study and the RF obtained previously in the method range study was calculated (Table 5). For 65 of the 74 analytes, the difference was $\leq$25%, which is within the Method 8240 acceptance range for just the six calibration check compounds. The percent difference obtained in this study for the six calibration check compounds was $\leq$25% except for 1,1-dichloroethene (29% difference). A >35% difference was observed for only three analytes, trans-1,4-dichloro-2-butene (47%), dichlorodifluoromethane (46%), and trans-1,2-dichloroethene (36%).
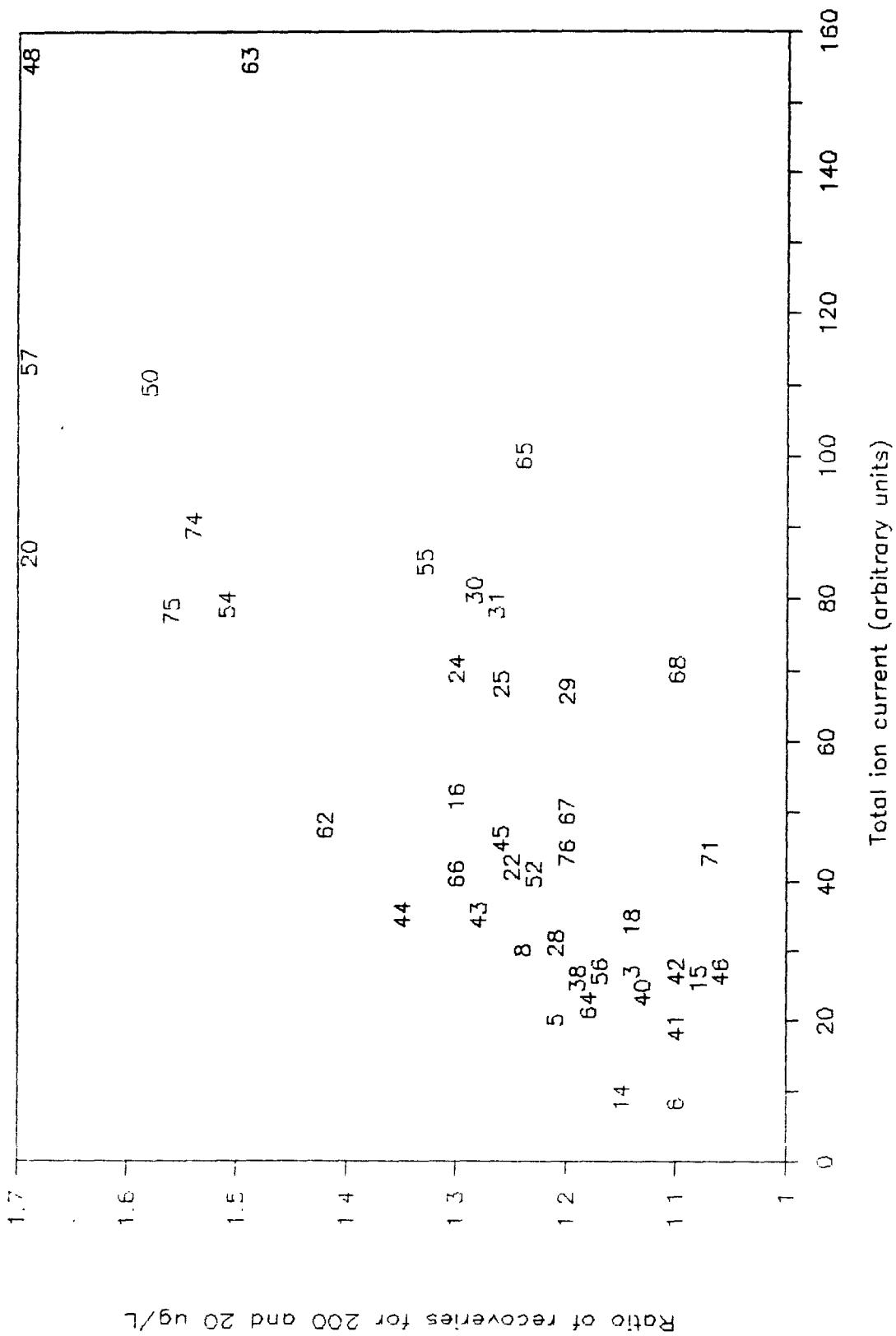
Figure 1. Effect of MS source ion concentration on changes in measured analyte recovery (ideal ratio = 1; the numbers refer to analytes as listed in Table 1).

TABLE 1. INFORMATION ABOUT ANALYTES EVALUATED IN METHOD RANGE STUDY

Analyte	IS[a]	CASRN	Source[b]	Retention Time[c]	MW	Quant. Ion m/z	Quant. Ion Rel. Int.
1 Acetone	1	67-64-1	EPA	8:02	58	43	100
2 Acrolein	1	107-02-8	ALD	7:52	56	56	100
3 Acrylonitrile	1	107-13-1	EPA	9:46	53	53	100
4 Allyl chloride	1	107-05-1	ALD	8:57	76	41	100
5 Benzene	2	71-43-2	SUP	14:00	78	78	100
6 Bis-(2-chloroethyl) ether	3	111-44-4	EPA	25:43	142	93	100
7 Bromobenzene	3	108-86-1	EAS	23:49	156	77	100
8 Bromodichloromethane	2	75-27-4	SUP	16:07	162	83	100
9 Bromomethane	1	74-83-9	SUP	5:52	94	94	100
10 2-Butanone	1	78-93-3	EPA	11:56	72	72	25
11 n-Butylbenzene	3	104-51-8	CHM	26:39	134	91	100
12 sec-Butylbenzene	3	135-98-8	ALD	25:23	134	105	100
13 tert-Butylbenzene	3	75-64-9	MCB	24:50	134	119	100
14 Carbon disulfide	1	75-15-0	MCB	8:52	76	76	100
15 Carbon tetrachloride	2	56-23-5	SUP	13:34	152	117	100
16 Chlorobenzene	3	108-90-7	SUP	20:52	112	112	100
17 2-Chloro-1,3-butadiene	1	126-99-8	P&B	12:03	88	53	100
18 Chlorodibromomethane	3	124-48-1	SUP	19:37	206	127	65
19 Chloroethane	1	75-00-3	SUP	6:05	64	64	100
20 2-Chloroethyl ethyl ether	2	628-34-2	ALD	17:01	108	59	100
21 Chloroform	1	67-66-3	SUP	12:25	118	83	100
22 1-Chlorohexane	3	544-10-5	ALD	20:24	118	91	100
23 Chloromethane	1	74-87-3	SUP	4:54	50	50	100
24 2-Chlorotoluene	3	95-49-8	EPA	24:00	126	126	25
25 4-Chlorotoluene	3	106-43-4	EPA	24:15	126	126	25
26 1,2-Dibromo-3-chloropropane	3	96-12-8	EPA	28:50	234	157	80
27 1,2-Dibromoethane	3	106-93-4	EPA	20:02	186	107	100
28 Dibromomethane	2	74-95-3	ALD	16:14	172	93	100
29 1,2-Dichlorobenzene	3	95-50-1	EPA	26:59	146	146	100
30 1,3-Dichlorobenzene	3	541-73-1	EPA	25:56	146	146	100
31 1,4-Dichlorobenzene	3	106-46-7	EPA	26:11	146	146	100
32 trans-1,4-Dichloro-2-butene	3	110-57-6	ALD	23:59	124	75	100
33 Dichlorodifluoromethane	1	75-71-8	SUP	4:34	120	85	100
34 1,1-Dichloroethane	1	75-34-3	SUP	10:48	98	63	100
35 1,2-Dichloroethane	2	107-06-2	SUP	14:06	98	62	100
36 1,1-Dichloroethene	1	75-35-4	SUP	7:59	96	96	60
37 cis-1,2-Dichloroethene	1	156-59-2	EPA	12:08	96	96	90
38 trans-1,2-Dichloroethene	1	156-60-5	SUP	9:47	96	96	90
39 Dichloromethane	1	75-09-2	SUP	9:15	84	84	85
40 1,2-Dichloropropane	2	78-87-5	SUP	15:38	112	76	65
41 1,3-Dichloropropane	3	142-28-9	ALD	19:11	112	76	100
42 1,1-Dichloropropene	1	563-58-6	ALD	13:25	110	75	100
43 cis-1,3-Dichloropropene	2	10061-01-5	SUP	17:18	110	75	100
44 trans-1,3-Dichloropropene	2	10061-02-6	SUP	18:23	110	75	100

(continued)

TABLE 1.

	Analyte	IS[a]	CASRN	Source[b]	Retention Time[c]	MW	Quant. Ion m/z	Quant. Ion Rel. Int.
45	1,2-Dimethylbenzene	3	95-47-6	EPA	22:05	106	106	45
46	1,4-Dimethylbenzene	3	106-42-3	EPA	21:10	106	106	45
47	Ethylbenzene	3	100-41-4	SUP	20:58	106	106	30
48	Ethyl methacrylate	2	97-63-2	ALD	18:26	114	69	100
49	Hexachlorobutadiene	3	87-68-3	EPA	31:07	258	225	100
50	Hexachloroethane	3	67-72-1	EPA	27:38	234	117	100
51	Hexachloropropene	3	1888-71-7	ALD	31:07	246	143	92
52	2-Hexanone	2	591-78-6	ALD	18:46	100	43	100
53	Iodomethane	1	74-88-4	ALD	8:37	142	142	100
54	Isopropylbenzene	3	98-82-8	ALF	22:53	120	105	100
55	p-Isopropyltoluene	3	99-87-6	ALD	25:50	134	119	100
56	Methacrylonitrile	1	126-98-7	ALD	12:28	67	41	100
57	Methyl methacrylate	2	80-62-6	ALD	15:58	100	69	85
58	4-Methyl-2-pentanone	2	108-10-1	ALD	16:59	100	43	100
59	Naphthalene	3	91-20-3	EPA	31:22	128	128	100
60	Propionitrile	1	107-12-0	ALD	12:11	55	54	100
61	n-Propylbenzene	3	103-65-1	ALD	23:47	120	91	100
62	Styrene	3	100-42-5	EPA	22:13	104	104	100
63	1,1,1,2-Tetrachloroethane	3	630-20-6	EPA	20:58	166	131	100
64	1,1,2,2-Tetrachloroethane	3	79-34-5	SUP	23:26	166	83	100
65	Tetrachloroethene	3	127-18-4	SUP	19:04	164	164	75
66	Toluene	2	108-88-3	SUP	17:49	92	92	65
67	Tribromomethane	3	75-25-2	SUP	22:55	250	173	100
68	1,2,4-Trichlorobenzene	3	120-82-1	EPA	30:47	180	180	100
69	1,1,1-Trichloroethane	1	71-55-6	SUP	13:06	132	97	100
70	1,1,2-Trichloroethane	2	79-00-5	SUP	18:39	132	97	100
71	Trichloroethene	2	79-01-6	SUP	15:12	130	130	97
72	Trichlorofluoromethane	1	75-69-4	SUP	4:32	136	101	100
73	1,2,3-Trichloropropane	3	96-18-4	EPA	23:44	146	110	30
74	1,2,4-Trimethylbenzene	3	95-63-6	CHS	25:06	120	105	100
75	1,3,5-Trimethylbenzene	3	108-67-8	ALD	23:47	120	105	100
76	Vinyl acetate	1	108-05-4	ALD	11:01	86	43	100
77	Vinyl chloride	1	75-01-4	SUP	5:08	62	62	100

[a]Internal standard 1 = bromochloromethane, 2 = 1,4-difluorobenzene, and 3 = chlorobenzene-d_5. [b]ALD = Aldrich, ALF = Alfa Chemical, CHM = Chemical Samples Co., CHS = Chmical Services, EAS = Eastman Kodak, EPA = USEPA Respository, MCB = Matheson, Colemn, and Bell, P&B = Pfaltz and Bauer, and SUP = Supelco. [c]Retention time in minutes and seconds.

TABLE 2. LINEAR RANGE RESPONSE FACTOR DATA FROM METHOD RANGE STUDY[a]

	Average response factor (% RSD) at given concentration, μg/L															
	5500	3000	1700	1000	550	300	170	100	55	30	17	10	5.5	3.0	1.0	Mean[b]
Acetone[c]	0.08 (12)	0.12 (15)	0.16 (24)	0.28 (16)	0.09 (21)	0.05 (12)	0.07 (31)									0.12 (63)
Acrolein[c]	0.04 (5)	0.04 (14)	0.04 (5)	0.04 (8)	0.06 (8)	0.04 (6)	0.06 (9)	0.03 (18)								0.05 (25)
Acrylonitrile[c]	0.10 (4)	0.08 (13)	0.07 (7)	0.07 (12)	0.11 (8)	0.08 (8)	0.11 (8)									0.09 (21)
Allyl chloride					1.34 (4)	1.21 (9)	0.71 (8)	0.72 (10)	1.16 (7)	0.92 (19)	1.24 (17)	1.01 (15)				1.04 (25)
Benzene					0.67 (2)	0.70 (5)	0.57 (3)	0.61 (4)	0.71 (3)	0.62 (4)	0.72 (5)	0.66 (9)	0.81 (3)	0.80 (13)		0.69 (13)
Bis-(2-chloroethyl) ether[c]	0.02 (5)	0.03 (4)	0.03 (5)		0.03 (7)	0.02 (7)	0.03 (4)	0.02 (6)	0.03 (7)							0.03 (10)
Bromobenzene							1.48 (8)	1.18 (4)	1.32 (3)	1.06 (6)	1.17 (2)	0.96 (7)	1.35 (12)	1.13 (16)		1.21 (16)
Bromodichloromethane					0.66 (2)	0.87 (6)	0.71 (2)	0.67 (5)	0.75 (4)	0.67 (6)	0.72 (3)	0.66 (6)	0.69 (2)	0.81 (5)		0.72 (10)
Bromomethane					0.90 (4)	1.05 (10)	0.83 (7)	0.94 (9)	1.03 (6)	1.01 (7)	1.29 (9)	1.17 (8)	1.65 (14)			1.10 (24)
2-Butanone[c]	0.05 (3)	0.05 (11)	0.04 (10)	0.05 (6)	0.06 (3)	0.04 (8)	0.06 (7)	0.04 (22)								0.05 (18)
n-Butylbenzene							1.44 (2)	1.43 (4)	1.63 (3)	1.48 (4)	1.45 (4)	1.40 (4)	1.78 (2)	1.69 (3)	1.99 (13)	1.58 (13)

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(continued)

TABLE 2.

	Average response factor (% RSD) at given concentration, µg/L															
	5500	3000	1700	1000	550	300	170	100	55	30	17	10	5.5	3.0	1.0	Mean[b]
sec-Butylbenzene							2.00 (2)	2.05 (3)	2.23 (3)	2.02 (3)	2.00 (6)	2.05 (3)	2.41 (3)	2.30 (3)	2.30 (12)	2.15 (9)
tert-Butylbenzene							3.12 (3)	3.08 (3)	3.06 (3)	2.95 (2)	2.89 (3)	3.12 (2)	3.35 (2)	3.28 (4)	2.90 (25)	3.08 (9)
Carbon disulfide					3.44 (3)	3.21 (10)	2.26 (8)	2.56 (7)	3.58 (4)	2.61 (9)	3.26 (7)	2.65 (8)	4.23 (3)	3.01 (10)		3.08 (19)
Carbon tetrachloride					0.51 (2)	0.72 (5)	0.62 (4)	0.62 (3)	0.64 (5)	0.68 (4)	0.59 (7)	0.67 (6)	0.63 (4)	0.76 (9)		0.64 (12)
Chlorobenzene						1.07 (4)	0.96 (2)	1.00 (1)	1.04 (2)	0.93 (3)	0.99 (1)	0.98 (2)	1.12 (2)	1.09 (5)		1.02 (6)
2-Chloro-1,3-butadiene					0.12 (6)	0.16 (14)	0.27 (11)	0.34 (7)	0.52 (8)	0.64 (16)	0.91 (8)	1.07 (14)	1.30 (11)			0.59[d] (69)
Chlorodibromomethane					0.42 (3)	0.61 (5)	0.56 (1)	0.55 (1)	0.54 (3)	0.51 (5)	0.51 (2)	0.51 (2)	0.47 (4)	0.58 (8)		0.53 (11)
Chloroethane					0.42 (2)	0.43 (9)	0.36 (7)	0.34 (10)	0.50 (8)	0.51 (7)						0.43 (16)
2-Chloroethyl ethyl ether[c]	0.12 (8)	0.09 (1)	0.08 (3)	0.10 (4)	0.07 (4)	0.09 (3)	0.06 (8)	0.09 (4)	0.07 (10)							0.09 (22)
Chloroform					2.72 (1)	2.99 (11)	2.52 (6)	2.44 (7)	3.06 (5)	2.59 (6)	2.97 (6)	2.64 (9)	3.44 (3)	3.44 (6)		2.88 (14)
1-Chlorohexane					0.53 (1)	0.60 (4)	0.47 (3)	0.48 (5)	0.58 (4)	0.52 (3)	0.53 (8)	0.52 (8)	0.64 (2)	0.73 (10)		0.56 (15)

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(continued)

TABLE 2.

	Average Response Factor (% RSD) at Given Concentration, µg/L															
	5500	3000	1700	1000	550	300	170	100	55	30	17	10	5.5	3.0	1.0	Mean[b]
Chloromethane					0.41 (5)	0.33 (11)	0.25 (6)	0.28 (9)	0.46 (5)	0.39 (16)						0.35 (23)
2-Chlorotoluene					0.47 (3)	0.48 (4)	0.44 (2)	0.49 (6)	0.47 (2)	0.45 (4)	0.48 (5)	0.49 (3)	0.52 (3)	0.48 (10)		0.48 (7)
4-Chlorotoluene					0.36 (4)	0.47 (5)	0.44 (2)	0.46 (3)	0.46 (2)	0.44 (4)	0.47 (2)	0.48 (2)	0.51 (1)	0.49 (6)		0.46 (9)
1,2-Dibromo-3-chloropropane					0.10 (3)	0.15 (6)	0.15 (3)	0.16 (7)	0.16 (6)	0.16 (5)	0.17 (8)	0.19 (6)				0.15 (16)
1,2-Dibromoethane					0.48 (2)	0.66 (5)	0.57 (2)	0.56 (2)	0.60 (3)	0.54 (3)	0.57 (2)	0.54 (3)	0.61 (4)	0.65 (7)		0.58 (10)
Dibromomethane					0.32 (2)	0.44 (6)	0.37 (2)	0.36 (3)	0.39 (4)	0.38 (5)	0.40 (3)	0.40 (5)	0.44 (4)	0.52 (10)		0.40 (14)
1,2-Dichlorobenzene						0.95 (5)	0.94 (2)	1.02 (4)	0.98 (2)	0.93 (4)	0.98 (2)	1.04 (5)	1.08 (4)	1.00 (3)		0.99 (6)
1,3-Dichlorobenzene						1.03 (4)	1.00 (2)	1.08 (3)	1.03 (1)	1.00 (4)	1.04 (2)	1.14 (5)	1.15 (4)	1.08 (6)		1.06 (6)
1,4-Dichlorobenzene						1.05 (5)	1.02 (2)	1.11 (3)	1.07 (3)	1.04 (4)	1.09 (2)	1.16 (5)	1.20 (2)	1.11 (4)		1.09 (6)
trans-1,4-Dichloro-2-butene[c]		0.09 (3)	0.07 (7)	0.07 (6)	0.05 (19)	0.05 (9)										0.07 (24)
Dichlorodifluoromethane									1.69 (17)	1.53 (15)	1.42 (24)	1.78 (22)	1.73 (8)	1.63 (20)		1.63 (20)

(continued)

TABLE 2.

	Average response factor (% RSD) at given concentration, µg/L															
	5500	3000	1700	1000	550	300	170	100	55	30	17	10	5.5	3.0	1.0	Mean[b]
1,1-Dichloroethane					1.83 (3)	1.73 (11)	1.31 (5)	1.30 (8)	1.93 (5)	1.53 (9)	1.87 (11)	1.69 (8)	2.68 (4)			1.76 (23)
1,2-Dichloroethane					0.33 (2)	0.41 (6)	0.32 (3)	0.32 (9)	0.39 (4)	0.34 (7)	0.36 (2)	0.31 (10)	0.40 (2)			0.35 (12)
1,1-Dichloroethene					1.02 (2)	1.03 (11)	0.85 (7)	0.96 (6)	1.20 (5)	1.05 (8)	1.23 (11)	1.19 (7)	1.56 (6)			1.12 (19)
cis-1,2-Dichloroethene					1.36 (1)	1.37 (11)	1.19 (5)	1.27 (7)	1.58 (4)	1.25 (6)	1.48 (5)	1.36 (6)	1.69 (7)			1.39 (13)
trans-1,2-Dichloroethene					1.19 (2)	1.16 (11)	0.97 (5)	1.10 (5)	1.37 (4)	1.08 (7)	1.28 (7)	1.10 (7)	1.45 (4)			1.19 (14)
Dichloromethane					1.03 (2)	1.02 (14)	0.84 (6)	0.91 (9)	1.19 (5)	0.94 (9)	1.21 (7)	1.17 (18)	1.70 (5)			1.11 (23)
1,2-Dichloropropane					0.13 (2)	0.17 (5)	0.14 (3)	0.14 (6)	0.16 (3)	0.15 (6)	0.16 (5)	0.15 (9)	0.22 (4)			0.16 (16)
1,3-Dichloropropane					0.47 (3)	0.55 (5)	0.45 (1)	0.43 (6)	0.53 (3)	0.41 (5)	0.48 (3)	0.40 (7)	0.59 (3)	0.49 (6)		0.48 (13)
1,1-Dichloropropene					0.43 (2)	0.49 (5)	0.36 (4)	0.37 (7)	0.47 (5)	0.40 (4)	0.42 (6)	0.39 (6)	0.53 (3)			0.43 (14)
cis-1,3-Dichloropropene					0.59 (2)	0.68 (7)	0.54 (4)	0.52 (6)	0.62 (3)	0.50 (6)	0.56 (2)	0.46 (6)	0.56 (5)			0.56 (12)
trans-1,3-Dichloropropene					0.30 (2)	0.37 (7)	0.31 (2)	0.29 (6)	0.33 (2)	0.26 (8)	0.29 (4)	0.22 (6)	0.26 (7)			0.29 (15)

(continued)

TABLE 2.

Average response factor (% RSD) at given concentration, μg/L

	5500	3000	1700	1000	550	300	170	100	55	30	17	10	5.5	3.0	1.0	Mean[b]
1,2-Dimethylbenzene					0.47 (3)	0.54 (4)	0.47 (2)	0.50 (2)	0.52 (2)	0.47 (4)	0.49 (2)	0.49 (3)	0.67 (3)	0.65 (8)	0.86 (7)	0.55 (20)
1,4-Dimethylbenzene					0.32 (2)	0.36 (4)	0.31 (2)	0.34 (3)	0.36 (4)	0.33 (3)	0.36 (3)	0.36 (5)				0.34 (6)
Ethylbenzene					0.45 (2)	0.57 (4)	0.48 (2)	0.50 (1)	0.52 (3)	0.47 (3)	0.49 (2)	0.48 (8)	0.69 (5)	0.67 (8)	0.90 (8)	0.55 (21)
Ethyl methacrylate[c]				0.34 (2)	0.36 (4)	0.27 (5)	0.31 (3)	0.24 (6)	0.36 (4)	0.26 (4)		0.35 (13)				0.31 (15)
Hexachlorobutadiene						0.63 (8)	0.59 (3)	0.66 (3)	0.66 (7)	0.82 (6)	0.57 (6)	0.85 (5)	0.70 (38)	1.01 (2)		0.72 (23)
Hexachloroethane					0.63 (2)	0.90 (5)	0.79 (2)	0.73 (3)	0.78 (3)	0.59 (12)	0.73 (3)	0.36 (15)	0.44 (12)			0.66 (25)
Hexachloropropene[c]		0.11 (6)	0.12 (3)	0.11 (5)	0.13 (5)	0.04 (60)	0.08 (9)									0.10[e] (32)
2-Hexanone[c]	0.09 (4)	0.10 (6)	0.08 (3)	0.07 (5)	0.10 (5)	0.08 (6)	0.09 (5)	0.07 (7)	0.12 (6)	0.09 (7)						0.09 (17)
Iodomethane					2.79 (1)	3.43 (7)	2.97 (5)	3.42 (7)	3.69 (6)	3.27 (7)	3.71 (5)	3.65 (5)	3.70 (11)			3.40 (12)
Isopropylbenzene						1.70 (4)	1.46 (2)	1.51 (2)	1.56 (3)	1.43 (3)	1.46 (3)	1.46 (2)	1.68 (2)	1.70 (4)		1.55 (7)
p-Isopropyltoluene						1.86 (5)	1.67 (1)	1.78 (2)	1.82 (2)	1.72 (4)	1.71 (4)	1.80 (2)				1.76 (5)
Methacrylonitrile	0.25 (2)	0.23 (14)	0.17 (8)	0.16 (8)	0.25 (5)	0.18 (9)	0.24 (10)	0.18 (11)	0.33 (9)	0.26 (10)						0.? (2)

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TABLE 2.

	Average response factor (% RSD) at given concentration, µg/L															
	5500	3000	1700	1000	550	300	170	100	55	30	17	10	5.5	3.0	1.0	Mean[b]
Methyl methacrylate[c]		0.15 (7)	0.12 (1)	0.11 (3)	0.13 (4)	0.10 (6)	0.12 (3)	0.10 (6)	0.14 (3)	0.11 (5)						0.12 (15)
4-Methyl-2-pentanone[c]			0.13 (1)	0.11 (4)	0.14 (5)	0.10 (5)	0.13 (6)	0.10 (5)	0.16 (4)	0.12 (7)						0.12 (17)
Naphthalene						0.92 (5)	0.95 (2)	1.06 (4)	1.08 (5)	0.98 (7)	1.10 (4)	1.13 (7)	0.91 (13)	1.11 (13)		1.03 (11)
Propionitrile[c]	0.03 (4)	0.03 (13)	0.03 (9)	0.03 (6)	0.05 (5)	0.03 (6)	0.04 (9)									0.03 (20)
n-Propylbenzene							1.97 (2)	1.93 (3)	2.05 (3)	1.77 (4)	1.84 (3)	1.73 (13)	2.13 (5)	2.20 (4)	2.42 (6)	2.00 (12)
Styrene						1.00 (5)	0.87 (1)	0.93 (2)	0.94 (2)	0.85 (4)	0.87 (3)	0.85 (2)	0.93 (3)	0.91 (3)		0.91 (6)
1,1,1-Tetrachloroethane						0.67 (4)	0.63 (3)	0.64 (2)	0.62 (2)	0.60 (3)	0.60 (2)	0.66 (3)	0.66 (4)	0.74 (7)		0.65 (7)
1,1,2-Tetrachloroethane					0.43 (3)	0.53 (6)	0.46 (1)	0.43 (4)	0.52 (3)	0.43 (4)	0.51 (3)	0.41 (6)	0.55 (8)			0.47 (12)
Tetrachloroethene						0.48 (6)	0.49 (4)	0.52 (3)	0.49 (3)	0.54 (3)	0.47 (6)	0.74 (4)	0.70 (4)			0.55 (18)
Toluene					0.54 (2)	0.59 (7)	0.51 (3)	0.55 (4)	0.61 (2)	0.53 (3)	0.61 (2)	0.59 (5)	1.01 (2)			0.61 (23)
Tribromomethane						0.53 (6)	0.53 (2)	0.53 (5)	0.48 (4)	0.47 (5)	0.45 (2)	0.45 (7)	0.39 (6)	0.48 (9)		0.48 (11)

(continued)

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TABLE 2.

	Average response factor (% RSD) at given concentration, μg/L															
	5500	3000	1700	1000	550	300	170	100	55	30	17	10	5.5	3.0	1.0	Mean[b]
1,2,4-Trichlorobenzene						0.82 (5)	0.85 (2)	0.95 (5)	0.87 (4)	0.92 (4)	0.92 (2)	1.01 (6)	1.01 (3)	0.94 (7)		0.92 (8)
1,1,1-Trichloroethane					0.52 (2)	0.68 (5)	0.58 (4)	0.59 (4)	0.62 (4)	0.64 (4)	0.59 (4)	0.69 (5)	0.70 (3)	0.92 (6)		0.65 (17)
1,1,2-Trichloroethane					0.27 (2)	0.31 (7)	0.28 (2)	0.28 (3)	0.31 (3)	0.27 (4)	0.31 (3)	0.28 (4)	0.33 (2)			0.29 (8)
Trichloroethene					0.35 (1)	0.44 (5)	0.42 (2)	0.47 (4)	0.50 (4)	0.49 (3)	0.59 (10)	0.67 (12)	0.66 (6)	0.69 (11)		0.53 (22)
Trichlorofluoromethane						0.16 (13)	0.12 (8)	0.14 (13)	0.25 (18)	0.23 (15)						0.18 (31)
1,2,3-Trichloropropane					0.12 (3)	0.17 (6)	0.15 (2)	0.15 (2)	0.16 (3)	0.15 (6)	0.15 (4)					0.15 (11)
1,2,4-Trimethylbenzene						2.15 (12)	1.93 (8)	1.35 (1)	1.38 (2)	1.29 (5)	1.31 (2)	1.31 (4)	1.51 (3)	2.09 (17)		1.59 (24)
1,3,5-Trimethylbenzene						1.68 (4)	1.47 (5)	1.50 (4)	1.52 (3)	1.38 (4)	1.39 (3)	1.45 (2)	1.68 (3)	1.67 (5)		1.52 (8)
Vinyl acetate		1.07 (12)	0.93 (6)	0.80 (6)	1.33 (5)	0.75 (5)	1.09 (6)	0.63 (7)	1.30 (2)							0.99 (25)
Vinyl chloride					0.57 (5)	0.53 (11)	0.41 (8)	0.46 (6)	0.71 (6)	0.60 (6)	0.75 (9)	0.53 (10)	0.71 (4)			0.59 (20)

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[a]Based on analysis of eight replicates except for bis-(2-chloroethyl) ether (7 replicates), n-butylbenzene (6 replicates), dimethylbenzene (6 replicates), and ethylbenzene (4 replicates) at the lowest concentration reported. [b]Mean of all reported sl[...] experiment response factors. [c]All RFs for 2-chloro-1,3-butadiene retained to illustrate effect of concentration on measured [d]RSD of RFs for hexachloropropene was >25% because of highly imprecise results only at 300 ug/L.

TABLE 3. DETECTION LIMITS OBTAINED FROM METHOD RANGE STUDY

Analyte	Lower limit of linear range µg/L	Empirical EDL µg/L	Calculated MDL µg/L	Nondetect Conc. µg/L[a]
Acetone	170	170	200	100
Acrolein	100	55	10	30
Acrylonitrile	170	170	40	100
Allyl chloride	10	5.5	2	3.0
Benzene	3.0	3.0	0.2	1.0
Bis-(2-chloroethyl) ether	55	55	10	30
Bromobenzene	3.0	3.0	0.7	1.0
Bromodichloromethane	3.0	3.0	0.2	1.0
Bromomethane	5.5	5.5	2	3.0
2-Butanone	100	30	10	10
n-Butylbenzene	1.0	1.0	0.4	0.3
sec-Butylbenzene	1.0	1.0	0.4	0.3
tert-Butylbenzene	1.0	1.0	0.8	0.3
Carbon disulfide	3.0	3.0	0.3	1.0
Carbon tetrachloride	3.0	3.0	0.2	1.0
Chlorobenzene	3.0	3.0	0.3	1.0
2-Chloro-1,3-butadiene	5.5	5.5	2	3.0
Chlorodibromomethane	3.0	3.0	0.2	1.0
Chloroethane	30	17	5	10
2-Chloroethyl ethyl ether	30	30	9	10
Chloroform	3.0	3.0	0.1	1.0
1-Chlorohexane	3.0	3.0	0.1	1.0
Chloromethane	30	17	10	10
2-Chlorotoluene	3.0	3.0	0.3	1.0
4-Chlorotoluene	3.0	3.0	0.3	1.0
1,2-Dibromo-3-chloropropane	10	10	2	5.5
1,2-Dibromoethane	3.0	3.0	0.2	1.0
Dibromomethane	3.0	3.0	0.2	1.0
1,2-Dichlorobenzene	3.0	3.0	0.5	1.0
1,3-Dichlorobenzene	3.0	3.0	0.4	1.0
1,4-Dichlorobenzene	3.0	3.0	0.5	1.0
trans-1,4-Dichloro-2-butene	170	55	30	30
Dichlorodifluoromethane	5.5	5.5	1	3.0
1,1-Dichloroethane	5.5	5.5	0.7	3.0
1,2-Dichloroethane	5.5	5.5	0.4	3.0
1,1-Dichloroethene	5.5	5.5	1	3.0
cis-1,2-Dichloroethene	5.5	5.5	1	3.0
trans-1,2-Dichloroethene	5.5	5.5	0.7	3.0
Dichloromethane	5.5	5.5	0.8	3.0
1,2-Dichloropropane	5.5	5.5	0.7	3.0

(continued)

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TABLE 3.

Analyte	Lower limit of linear range µg/L	Empirical EDL µg/L	Calculated MDL µg/L	Nondetect Conc. µg/L[a]
1,3-Dichloropropane	3.0	3.0	0.3	1.0
1,1-Dichloropropene	5.5	5.5	0.5	3.0
cis-1,3-Dichloropropene	5.5	5.5	0.9	3.0
trans-1,3-Dichloropropene	5.5	5.5	1	3.0
1,2-Dimethylbenzene	1.0	1.0	0.2	0.3
~ethylbenzene	10	1.0	0.6	0.3
Ethyl methacrylate	10	10	7	3.0
Ethylbenzene	1.0	1.0	0.4	0.3
Hexachlorobutadiene	3.0	3.0	0.7	1.0
Hexachloroethane	5.5	5.5	2	3.0
Hexachloropropene	170	170	50	100
2-Hexanone	30	30	6	17
Iodomethane	5.5	5.5	2	3.0
Isopropylbenzene	3.0	3.0	0.4	0.3
p-Isopropyltoluene	10	10	0.7	5.5
Methacrylonitrile	30	30	9	17
Methyl methacrylate	30	30	5	3.0
4-Methyl-2-pentanone	30	30	6	17
Naphthalene	3.0	3.0	0.5	1.0
Propionitrile	170	170	40	100
n-Propylbenzene	1.0	1.0	0.2	0.3
Styrene	3.0	3.0	0.4	1.0
1,1,1,2-Tetrachloroethane	3.0	3.0	0.2	1.0
1,1,2,2-Tetrachloroethane	5.5	5.5	1	3.0
Tetrachloroethene	3.0	3.0	0.2	1.0
Toluene	3.0	3.0	0.2	0.3
Tribromomethane	3.0	3.0	0.3	1.0
1,2,4-Trichlorobenzene	3.0	3.0	0.3	1.0
1,1,1-Trichloroethane	3.0	3.0	0.2	1.0
1,1,2-Trichloroethane	5.5	5.5	0.3	3.0
Trichloroethene	3.0	3.0	0.1	0.3
Trichlorofluoromethane	30	30	10	17
1,2,3-Trichloropropane	17	17	2	10
1,2,4-Trimethylbenzene	3.0	3.0	1	1.0
1,3,5-Trimethylbenzene	3.0	3.0	0.3	1.0
Vinyl acetate	55	55	4	30
Vinyl chloride	5.5	5.5	0.6	3.0

[a]Nondetect concentration = the highest concentration studied at which the analyte was not detected.

TABLE 4. ACCURACY AND PRECISION OF ANALYTE[a] MEASUREMENTS IN SPIKED AND UNSPIKED SAMPLES

Analyte	Unspiked Meas. Conc. (µg/L)	POTW Sludge Leachate High Bias,% (RSD)	POTW Sludge Leachate Low Bias,% (RSD)	Water With Fulvic Acid High Bias,% (RSD)	Water With Fulvic Acid Low Bias,% (RSD)
Acrolein[c]		-1 (12)	0 (7)	-10 (12)	15 (5)
Acrylonitrile[c]		12 (8)	-2 (12)	6 (8)	-7 (4)
Allyl chloride		-1 (30)	22 (8)	24 (8)	20 (10)
Benzene	7.5	12 (4)	3 (6)	25 (3)	4 (6)
Bis-(2-chloroethyl) ether[c]		0 (6)	2 (10)	-11 (10)	3 (10)
Bromobenzene[d]	1.9	48 (3)	-17 (4)	65 (4)	-4 (6)
Bromodichloromethane		17 (3)	-1 (3)	26 (2)	2 (3)
Bromomethane[d]		62 (38)	37 (14)	81 (10)	50 (10)
2-Butanone[c]		-5 (7)	-11 (25)	-9 (6)	-5 (8)
n-Butylbenzene[d]	Trace	20 (4)	0 (5)	49 (6)	3 (3)
sec-Butylbenzene[d]	6.2	-1 (5)	-33 (5)	35 (4)	2 (2)
tert-Butylbenzene[d]	Trace	-5 (3)	-5 (3)	20 (5)	-4 (2)
Carbon disulfide		16 (11)	16 (10)	28 (8)	13 (5)
Carbon tetrachloride		14 (5)	1 (6)	22 (2)	13 (3)
Chlorobenzene	7.1	26 (3)	3 (2)	35 (3)	4 (2)
Chlorodibromomethane		13 (4)	-7 (7)	13 (4)	-1 (7)
Chloroethane[e]		32 (39)	38 (11)	93 (11)	23 (23)
2-Chloroethyl ethyl ether[c]		30 (8)	-18 (10)	25 (13)	-22 (15)
Chloroform		26 (7)	10 (4)	27 (5)	19 (6)
1-Chlorohexane		20 (4)	0 (9)	32 (3)	7 (8)
Chloromethane		28 (23)	34 (22)	2 (7)	33 (23)
2-Chlorotoluene[d]		26 (4)	59 (9)	21 (29)	3 (3)
4-Chlorotoluene		29 (4)	3 (5)	36 (4)	6 (3)
1,2-Dibromoethane		5 (5)	-4 (4)	5 (5)	-4 (6)
Dibromomethane		11 (5)	-1 (4)	13 (3)	-1 (4)
1,2-Dibromo-3-chloropropane		-17 (5)	-5 (12)	-18 (9)	-7 (17)
1,2-Dichlorobenzene		12 (3)	0 (4)	21 (4)	1 (5)
1,3-Dichlorobenzene	Trace	20 (3)	-2 (3)	32 (4)	2 (3)
1,4-Dichlorobenzene	1.7	18 (2)	2 (3)	33 (4)	4 (4)
Dichlorodifluoromethane[d]	7.1	30 (55)	64 (24)	3 (20)	33 (35)
1,1-Dichloroethane		22 (7)	19 (8)	27 (9)	19 (10)
1,2-Dichloroethane		1 (5)	-3 (2)	9 (4)	-1 (7)
1,1-Dichloroethene		10 (10)	15 (13)	14 (11)	22 (10)
cis-1,2-Dichloroethene		20 (7)	5 (6)	26 (7)	14 (3)
trans-1,2-Dichloroethene		20 (9)	10 (8)	33 (8)	12 (6)
Dichloromethane	6.0	16 (8)	67 (4)	15 (8)	22 (4)
1,2-Dichloropropane		26 (13)	5 (6)	18 (2)	8 (3)
1,3-Dichloropropane		4 (4)	-5 (4)	8 (4)	1 (6)
1,1-Dichloropropene		6 (6)	2 (7)	22 (3)	11 (4)
cis-1,3-Dichloropropene	3.7	22 (4)	-22 (3)	27 (4)	-1 (2)

(continued)

TABLE 4. ACCURACY AND PRECISION OF ANALYTE[a] MEASUREMENTS IN SPIKED AND UNSPIKED SAMPLES

		POTW Sludge Leachate		Water With Fulvic Acid	
			Spike Concentration[b]		
	Unspiked	High	Low	High	Low
	Meas. Conc.	Bias,%	Bias,%	Bias,%	Bias,%
Analyte	(μg/L)	(RSD)	(RSD)	(RSD)	(RSD)
trans-1,3-Dichloropropene		20 (5)	-8 (4)	23 (5)	-9 (7)
trans-1,4-Dichloro-2-butene[c,d]		72 (15)	-52 (14)	50 (13)	-59 (15)
1,2-Dimethylbenzene	4.4	22 (2)	0 (4)	30 (4)	4 (3)
1,4-Dimethylbenzene	13	9 (3)	3 (3)	20 (4)	13 (3)
Ethyl methacrylate[c,d]		-6 (3)	-24 (4)	7 (4)	-27 (10)
Ethylbenzene		62 (4)	19 (4)	77 (4)	4 (2)
Hexachlorobutadiene	Trace	5 (12)	7 (14)	23 (12)	4 (10)
Hexachloroethane		60 (6)	3 (4)	60 (6)	0 (7)
Hexachloropropene[c]	Trace	83 (5)	-46 (40)	92 (8)	-9 (19)
2-Hexanone[c]	Trace	36 (24)	-14 (8)	2 (12)	-18 (13)
Iodomethane		10 (9)	12 (4)	20 (11)	15 (5)
Isopropylbenzene		26 (2)	1 (4)	51 (4)	0 (3)
p-Isopropyltoluene	Trace	10 (3)	-2 (3)	34 (5)	0 (3)
Methacrylonitrile[c]	Trace	-55 (55)	-16 (8)	11 (6)	-5 (5)
Methyl methacrylate[c]		34 (6)	-18 (6)	39 (11)	-17 (10)
4-Methyl-2-pentanone[c,d]	Trace	-24 (51)	-47 (5)	15 (12)	-16 (10)
Naphthalene	2.8	-8 (7)	44 (8)	-5 (7)	-2 (10)
Propionitrile[c]		-3 (9)	-6 (12)	-2 (8)	-6 (5)
n-Propylbenzene[d]	1.2	22 (2)	10 (3)	57 (4)	-5 (2)
Styrene		29 (3)	-3 (3)	36 (4)	-4 (5)
1,1,1,2-Tetrachloroethane		43 (2)	-2 (3)	48 (3)	-1 (3)
1,1,2,2-Tetrachloroethane		-8 (6)	-7 (5)	-5 (9)	-7 (8)
Tetrachloroethene		15 (4)	-4 (6)	25 (5)	1 (1)
Toluene	19	33 (2)	8 (2)	37 (4)	5 (3)
Tribromomethane		11 (5)	-11 (8)	8 (6)	-10 (11)
1,2,4-Trichlorobenzene		5 (4)	7 (6)	15 (5)	3 (7)
1,1,1-Trichloroethane		7 (5)	7 (6)	14 (3)	21 (3)
1,1,2-Trichloroethane		5 (5)	-7 (4)	8 (5)	0 (8)
Trichloroethene		9 (3)	9 (3)	20 (2)	12 (3)
1,2,3-Trichloropropane		5 (5)	-5 (6)	4 (7)	-8 (9)
1,2,4-Trimethylbenzene	1.4	36 (3)	56 (4)	56 (4)	0 (2)
1,3,5-Trimethylbenzene		-13 (5)	8 (3)	59 (19)	2 (2)
Vinyl acetate[c]		-29 (29)	-1 (5)	19 (6)	-5 (4)
Vinyl chloride		26 (52)	26 (12)	-6 (10)	33 (7)
Mean		16 (10)	3 (7)	25 (7)	3 (7)

[a] Data for acetone, 2-chloro-1,3-butadiene, and trichlorofluoromethane not included, because those compounds did not have acceptable linear ranges. [b] Except for poorly purged analytes, high concentration was 200 ug/L, and low concentration was 20 ug/L. For poorly purged compounds, high concentration was 2000 ug/L, and low concentration was 200 ug/L. [c] Poorly purged compound. [d] High concentration outside of linear range. [e] Low concentration outside of linear range.

TABLE 5. CALIBRATION DATA FROM MATRIX VALIDATION STUDIES

Analyte(b) Diff.(d)	Response factor (% RSD) obtained on given day (a)							Average RF (% RSD) from Table 2	Percent
	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Average		
Acrolein(c)	0.04 (13)	0.04 (9)	0.04 (18)	0.04 (12)	0.05 (13)	0.05 (1)	0.04 (15)	0.05 (25)	1
Acrylonitrile(c)	0.08 (11)	0.08 (13)	0.08 (9)	0.08 (8)	0.09 (5)	0.09 (3)	0.08 (12)	0.09 (21)	6
Allyl chloride	1.12 (7)	1.15 (4)	1.24 (10)	1.20 (4)	1.27 (6)	0.71(54)	1.11 (23)	1.04 (25)	7
Benzene	0.58 (4)	0.61 (6)	0.59 (6)	0.64 (4)	0.66 (1)	0.64 (4)	0.62 (6)	0.69 (13)	10
Bis-(2-chloroethyl) ether(c)	0.02 (24)	0.02 (9)	0.02 (10)	0.03 (13)	0.02 (6)	0.02 (7)	0.02 (20)	0.03 (10)	22
Bromobenzene	1.19 (9)	1.13 (6)	1.11 (6)	1.31 (1)	1.32 (1)	1.22 (3)	1.21 (8)	1.21 (16)	0
Bromodichloromethane	0.61 (8)	0.58 (6)	0.54 (9)	0.64 (6)	0.63 (1)	0.60 (2)	0.60 (8)	0.72 (10)	20
Bromomethane	0.94 (22)	0.76 (3)	0.88 (22)	0.73 (6)	0.82 (9)	0.87 (4)	0.84 (17)	1.10 (24)	31
2-Butanone(c)	0.04 (15)	0.04 (9)	0.04 (7)	0.04 (8)	0.05 (6)	0.05 (7)	0.04 (11)	0.05 (18)	15
n-Butylbenzene	1.36 (7)	1.35 (2)	1.32 (2)	1.58 (1)	1.51 (4)	1.42 (2)	1.42 (7)	1.58 (13)	11
sec-Butylbenzene	1.96 (7)	2.05 (3)	1.99 (2)	2.33 (1)	2.15 (4)	2.05 (1)	2.09 (7)	2.15 (9)	3
tert-Butylbenzene	3.20 (7)	3.26 (4)	3.18 (4)	3.57 (1)	3.38 (1)	3.32 (2)	3.32 (5)	3.08 (9)	7
Carbon disulfide	2.46 (10)	2.42 (5)	2.49 (9)	2.29 (6)	2.55 (13)	2.57 (4)	2.46 (9)	3.08 (19)	25
Carbon tetrachloride	0.63 (6)	0.59 (5)	0.54 (12)	0.65 (9)	0.61 (4)	0.59 (4)	0.60 (9)	0.64 (12)	7
Chlorobenzene	0.97 (6)	0.95 (5)	0.93 (4)	1.01 (1)	1.02 (1)	0.99 (0)	0.98 (5)	1.02 (6)	4
Chlorodibromomethane	0.56 (9)	0.49 (9)	0.43 (8)	0.54 (2)	0.53 (5)	0.51 (6)	0.51 (10)	0.53 (11)	3
Chloroethane	0.40 (2)	0.43 (19)	0.50 (7)	0.44 (7)	0.44 (16)	0.45 (16)	0.4 (15)	0.43 (16)	3
2-Chloroethyl ethyl ether(c)	0.09 (13)	0.09 (11)	0.08 (9)	0.10 (5)	0.10 (4)	0.09 (8)	0.09 (12)	0.09 (22)	7
Chloroform	2.29 (9)	2.21 (4)	2.36 (8)	2.30 (6)	2.43 (9)	2.44 (5)	2.34 (8)	2.88 (14)	23
1-Chlorohexane	0.47 (6)	0.45 (1)	0.46 (4)	0.51 (1)	0.49 (8)	0.49 (1)	0.48 (6)	0.56 (15)	18
Chloromethane	0.49 (26)	0.48 (8)	0.47 (8)	0.38 (7)	0.55 (9)	0.50 (8)	0.48 (17)	0.35 (23)	27
2-Chlorotoluene	0.45 (7)	0.45 (6)	0.45 (12)	0.48 (1)	0.48 (2)	0.48 (7)	0.46 (8)	0.48 (7)	4
4-Chlorotoluene	0.44 (5)	0.45 (4)	0.44 (7)	0.48 (1)	0.47 (5)	0.44 (3)	0.45 (6)	0.46 (9)	1
1,2-Dibromo-3-chloropropane	0.14 (15)	0.13 (11)	0.12 (13)	0.16 (3)	0.14 (6)	0.13 (6)	0.14 (13)	0.15 (16)	7
1,2-Dibromoethane	0.53 (10)	0.49 (8)	0.45 (8)	0.53 (1)	0.53 (3)	0.53 (2)	0.51 (9)	0.58 (10)	14
Dibromomethane	0.37 (5)	0.34 (10)	0.32 (10)	0.35 (1)	0.35 (1)	0.37 (3)	0.35 (8)	0.40 (14)	13
1,2-Dichlorobenzene	0.99 (7)	0.98 (5)	0.92 (5)	1.13 (2)	1.02 (3)	1.00 (4)	1.01 (8)	0.99 (6)	2
1,3-Dichlorobenzene	1.06 (7)	1.04 (5)	0.98 (5)	1.17 (1)	1.09 (2)	1.04 (3)	1.06 (7)	1.06 (6)	0
1,4-Dichlorobenzene	1.09 (7)	1.08 (7)	1.03 (8)	1.22 (0)	1.12 (3)	1.07 (5)	1.10 (8)	1.09 (6)	1
trans-1,4-Dichloro-2-butene(c)	0.06 (28)	0.04 (23)	0.03 (13)	0.06 (20)	0.05 (17)	0.03 (17)	0.05 (33)	0.07 (24)	47
Dichlorodifluoromethane	1.03 (15)	0.94 (30)	1.07 (6)	0.67 (14)	0.83 (37)	1.00 (23)	0.93 (27)	1.35 (33)	46
1,1-Dichloroethane	1.46 (14)	1.43 (7)	1.52 (6)	1.49 (5)	1.66 (6)	1.70 (7)	1.54 (10)	1.76 (23)	14

(continued)

TABLE 5.

| Analyte(b)	Response factor (% RSD) obtained on given day (a)							Average RF (% RSD) from Table 2	Percent Diff.(d)
	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Average		
1,2-Dichloroethane	0.34 (6)	0.34 (8)	0.33 (7)	0.39 (3)	0.38 (1)	0.35 (1)	0.36 (8)	0.35 (12)	1
cis-1,2-Dichloroethene	1.19 (8)	1.21 (6)	1.24 (10)	1.16 (2)	1.30 (11)	1.31 (4)	1.23 (9)	1.12 (19)	9
trans-1,2-Dichloroethene	0.99 (6)	1.02 (2)	1.05 (8)	0.97 (3)	1.05 (12)	1.07 (5)	1.02 (8)	1.39 (13)	36
1,1-Dichloroethane	0.92 (6)	0.93 (7)	0.99 (13)	0.83 (7)	0.93 (18)	0.95 (12)	0.92 (13)	1.19 (14)	29
Dichloromethane	0.80 (10)	0.81 (3)	0.83 (8)	0.98 (12)	0.83 (3)e	0.87 (6)	0.86 (11)	1.11 (23)	29
1,2-Dichloropropane	0.14 (7)	0.15 (6)	0.14 (7)	0.15 (3)	0.15 (3)	0.16 (6)	0.15 (7)	0.16 (16)	7
1,3-Dichloropropane	0.43 (9)	0.39 (9)	0.39 (4)	0.44 (2)	0.46 (4)	0.44 (2)	0.43 (8)	0.48 (13)	13
1,1-Dichloropropene	0.41 (4)	0.39 (2)	0.40 (5)	0.44 (7)	0.44 (4)	0.43 (2)	0.42 (7)	0.43 (14)	3
cis-1,3-Dichloropropene	0.50 (9)	0.48 (5)	0.46 (8)	0.51 (2)	0.52 (1)	0.50 (3)	0.50 (7)	0.56 (12)	13
trans-1,3-Dichloropropene	0.29 (13)	0.26 (8)	0.24 (10)	0.28 (3)	0.28 (4)	0.26 (4)	0.27 (10)	0.29 (15)	9
1,2-Dimethylbenzene	0.45 (8)	0.45 (7)	0.44 (4)	0.49 (3)	0.48 (4)	0.44 (1)	0.46 (6)	0.55 (20)	20
1,4-Dimethylbenzene	0.31 (7)	0.31 (2)	0.32 (5)	0.34 (1)	0.34 (1)	0.31 (1)	0.32 (6)	0.34 (6)	6
Ethyl methacrylate(c)	0.36 (10)	0.35 (12)	0.34 (10)	0.39 (1)	0.42 (4)	0.40 (6)	0.38 (11)	0.31 (15)	17
Ethylbenzene	0.50 (7)	0.50 (6)	0.50 (6)	0.55 (1)	0.48 (20)	0.51 (1)	0.51 (10)	0.55 (21)	8
Hexachlorobutadiene	0.74 (7)	0.81 (7)	0.71 (9)	1.02 (7)	0.73 (6)	0.74 (3)	0.79 (15)	0.72 (23)	9
Hexachloroethane	0.76 (16)	0.57 (15)	0.36 (24)	0.74 (19)	0.65 (10)	0.51 (20)	0.60 (29)	0.66 (25)	11
Hexachloropropene(c)	0.16 (45)	0.10 (57)	0.03 (27)	0.15 (57)	0.06 (39)	0.02 (14)	0.09 (86)	0.09 (35)	7
2-Hexanone(c)	0.14 (10)	0.14 (14)	0.13 (12)	0.11 (48)	0.17 (6)	0.13 (25)	0.13 (24)	0.09 (17)	32
Iodomethane	3.07 (9)	2.96 (4)	3.08 (9)	2.95 (4)	2.88 (9)	3.12 (2)	3.01 (7)	3.40 (12)	13
Isopropylbenzene	1.44 (9)	1.46 (5)	1.44 (5)	1.61 (1)	1.54 (1)	1.47 (2)	1.49 (6)	1.55 (8)	3
p-Isopropyltoluene	1.74 (5)	1.76 (4)	1.72 (3)	1.95 (2)	1.83 (2)	1.77 (1)	1.80 (5)	1.76 (5)	2
Methacrylonitrile(c)	0.24 (7)	0.25 (6)	0.25 (7)	0.15 (56)	0.29 (8)	0.28 (5)	0.24 (25)	0.22 (24)	8
Methyl methacrylate(c)	0.11 (9)	0.10 (11)	0.10 (8)	0.11 (2)	0.12 (1)	0.12 (4)	0.11 (9)	0.12 (16)	9
4-Methyl-2-pentanone(c)	0.16 (8)	0.16 (16)	0.15 (7)	0.19 (5)	0.19 (5)	0.18 (5)	0.17 (13)	0.12 (17)	28
Naphthalene	0.89 (19)	0.84 (10)	0.78 (8)	1.12 (4)	1.02 (9)	0.91 (9)	0.92 (16)	1.03 (11)	11
Propionitrile(c)	0.03 (17)	0.03 (10)	0.03 (10)	0.04 (9)	0.04 (7)	0.04 (5)	0.04 (12)	0.03 (20)	9
n-Propylbenzene	1.82 (7)	1.83 (4)	1.82 (5)	2.02 (1)	1.72 (21)	1.92 (3)	1.86 (10)	2.00 (12)	8
Styrene	0.80 (6)	0.83 (5)	0.79 (4)	0.87 (2)	0.89 (1)	0.83 (1)	0.84 (6)	0.91 (6)	9
1,1,1,2-Tetrachloroethane	0.65 (8)	0.63 (8)	0.57 (9)	0.70 (1)	0.67 (3)	0.63 (5)	0.64 (9)	0.63 (12)	2
1,1,2,2-Tetrachloroethane	0.43 (9)	0.39 (11)	0.37 (6)	0.47 (2)	0.47 (4)	0.44 (6)	0.43 (11)	0.47 (12)	11
Tetrachloroethene	0.57 (8)	0.60 (4)	0.59 (7)	0.66 (8)	0.60 (5)	0.66 (5)	0.61 (8)	0.53 (22)	14
Toluene	0.48 (6)	0.49 (4)	0.48 (5)	0.49 (3)	0.51 (3)	0.51 (2)	0.49 (5)	0.61 (23)	24

(continued)

TABLE 5.

| Analyte[b]	Response factor (% RSD) obtained on given day [a]							Average RF (% RSD) from Table 2	Percent Diff.[d]
	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Average		
Tribromomethane	0.56 (10)	0.51 (15)	0.41 (13)	0.59 (4)	0.52 (11)	0.50 (12)	0.51 (15)	0.46 (15)	10
1,2,4-Trichlorobenzene	0.91 (17)	0.91 (7)	0.81 (8)	1.17 (4)	0.94 (7)	0.89 (7)	0.94 (15)	0.88 (16)	6
1,1,1-Trichloroethane	0.77 (9)	0.83 (5)	0.96 (5)	0.84 (8)	0.88 (7)	0.86 (7)	0.86 (8)	0.65 (17)	24
1,1,2-Trichloroethane	0.27 (5)	0.26 (9)	0.24 (8)	0.27 (4)	0.28 (3)	0.27 (2)	0.27 (7)	0.29 (8)	11
Trichloroethene	0.49 (6)	0.48 (7)	0.47 (7)	0.52 (1)	0.50 (2)	0.48 (1)	0.49 (6)	0.53 (22)	8
1,2,3-Trichloropropane	0.14 (9)	0.13 (9)	0.12 (7)	0.15 (1)	0.14 (6)	0.14 (7)	0.14 (10)	0.15 (11)	10
1,2,4-Trimethylbenzene	1.22 (7)	1.26 (4)	1.24 (5)	1.42 (1)	1.32 (1)	1.26 (2)	1.29 (7)	1.59 (24)	23
1,3,5-Trimethylbenzene	1.96 (7)	2.05 (3)	1.99 (2)	2.74 (22)	2.99 (17)	2.05 (1)	2.30 (23)	1.52 (8)	34
Vinyl acetate[c]	1.11 (7)	1.15 (6)	1.16 (9)	0.68 (51)	1.43 (5)	1.36 (6)	1.15 (25)	0.99 (25)	14
Vinyl chloride	0.68 (11)	0.59 (7)	0.61 (10)	0.56 (10)	0.67 (9)	0.64 (6)	0.63 (12)	0.59 (20)	6

[a] Average RF from triplicate analysis each day of reagent water spiked with analytes at 50 µg/L, except as noted. POTW sludge leachate experiments were performed on Days 1-3, and water containing fulvic acid experiments were performed on Days 4-6. Unspiked, low concentration, and high concentration experiments for each matrix were performed on successive days. [b] Data for acetone, 2-chloro-1,3-butadiene, and trichlorofluoromethane not included because these compounds did not have an acceptable linear range in the method range study. [c] Analyte spiked into reagent water at 500 µg/L instead of 50 µg/L. [d] Percent Difference = 100 (Av. Daily RF - Av. Table 2 RF) / Av. Daily RF. [e] Average and RSD of two replicates instead of three.

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APPENDIX A

CALIBRATION CURVES FROM METHOD RANGE STUDIES

Acetone

Relative Peak Area vs. Analyte Concentration (ug/L) (Thousands)

Acrolein

Relative Peak Area vs. Analyte Concentration (ug/L)

A-1 ɑ
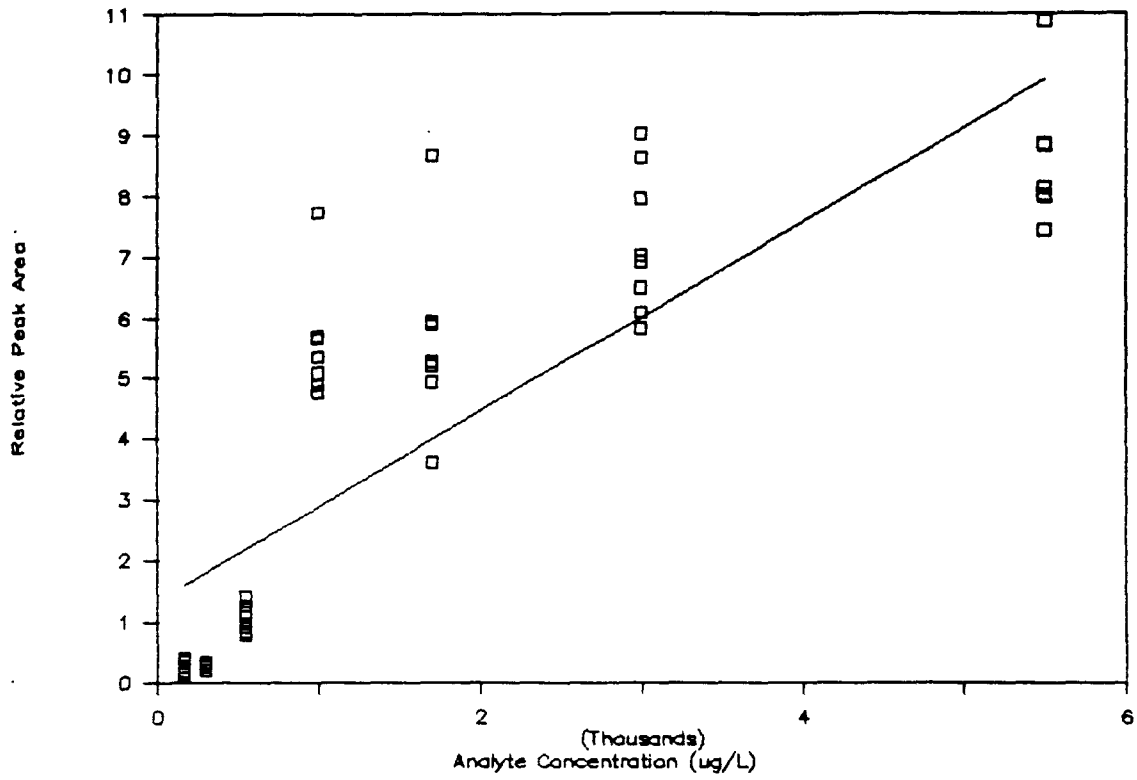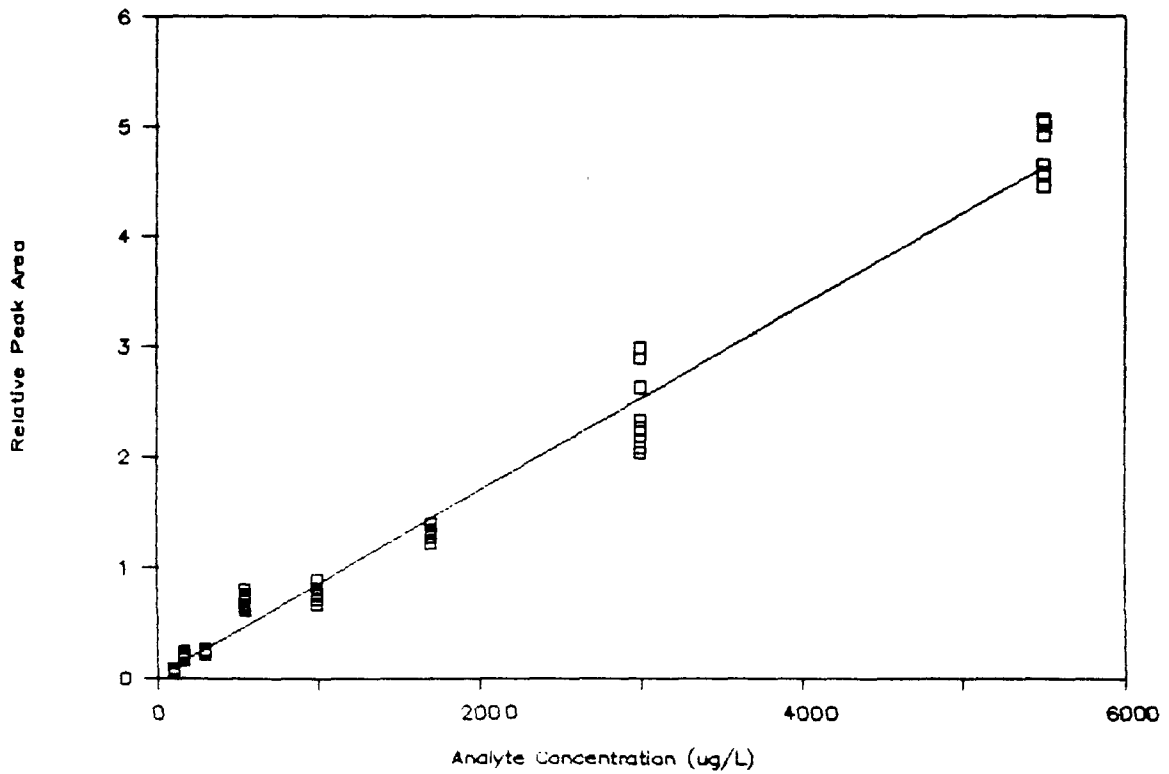
Acrylonitrile

Allyl chloride

A-2
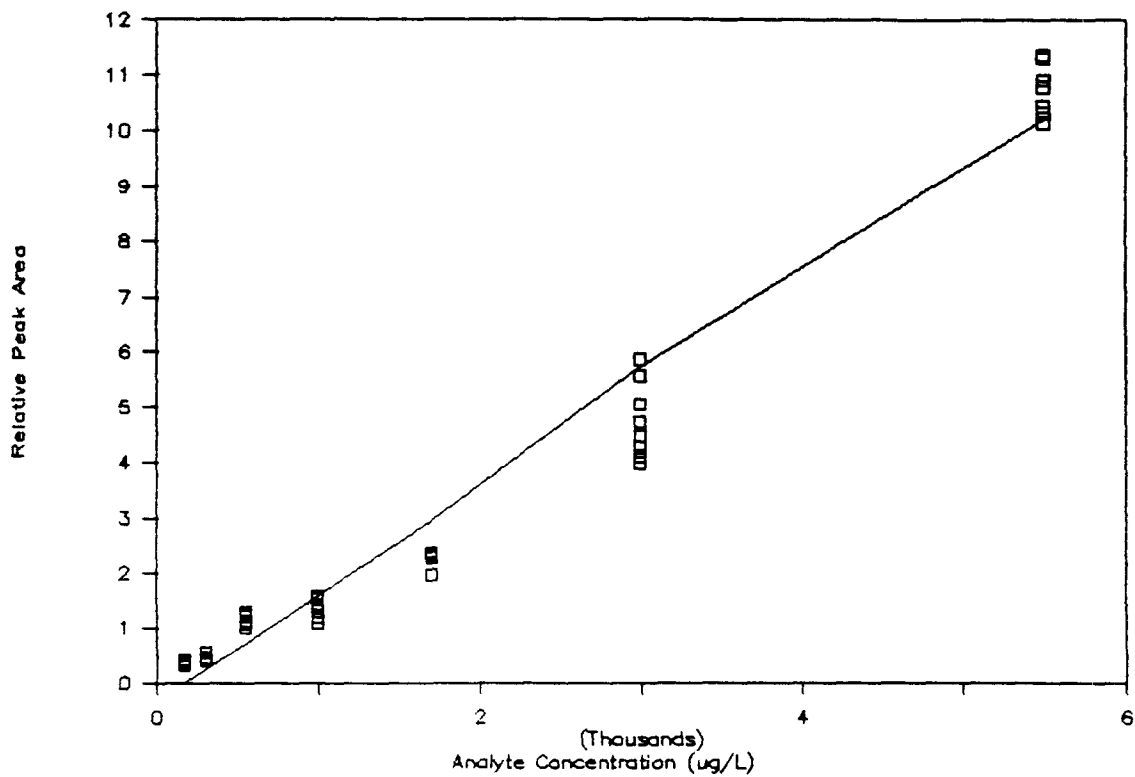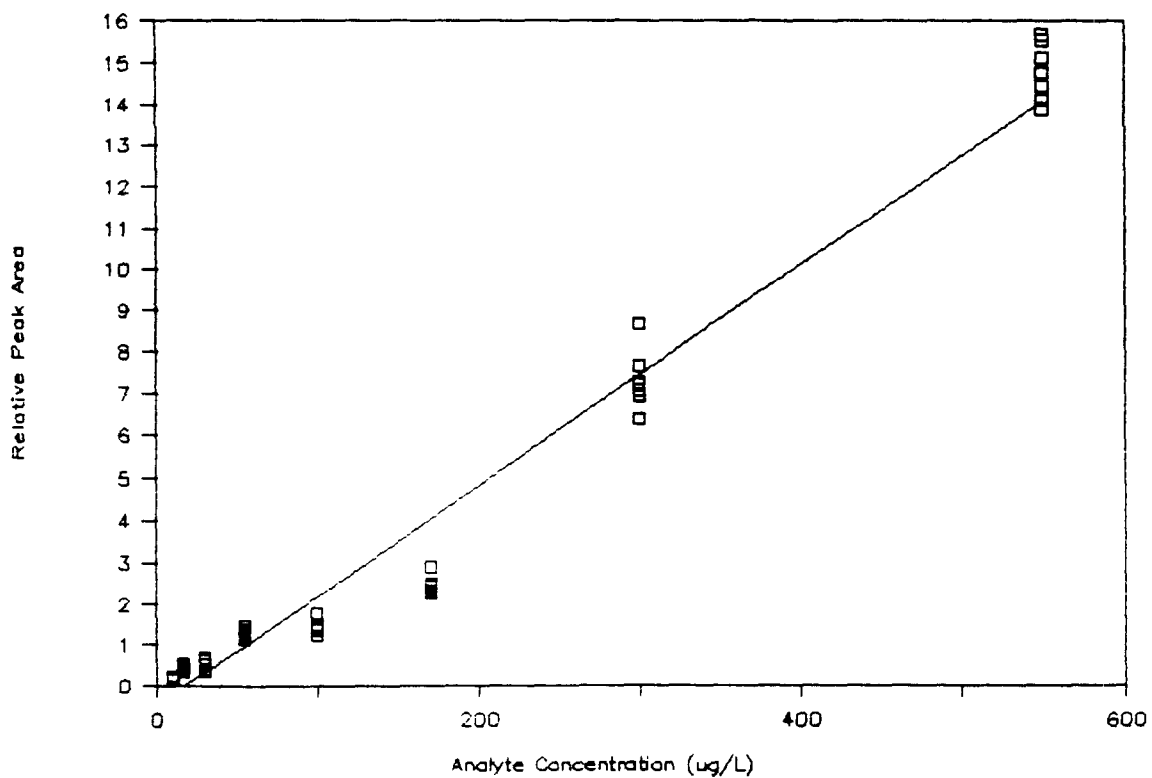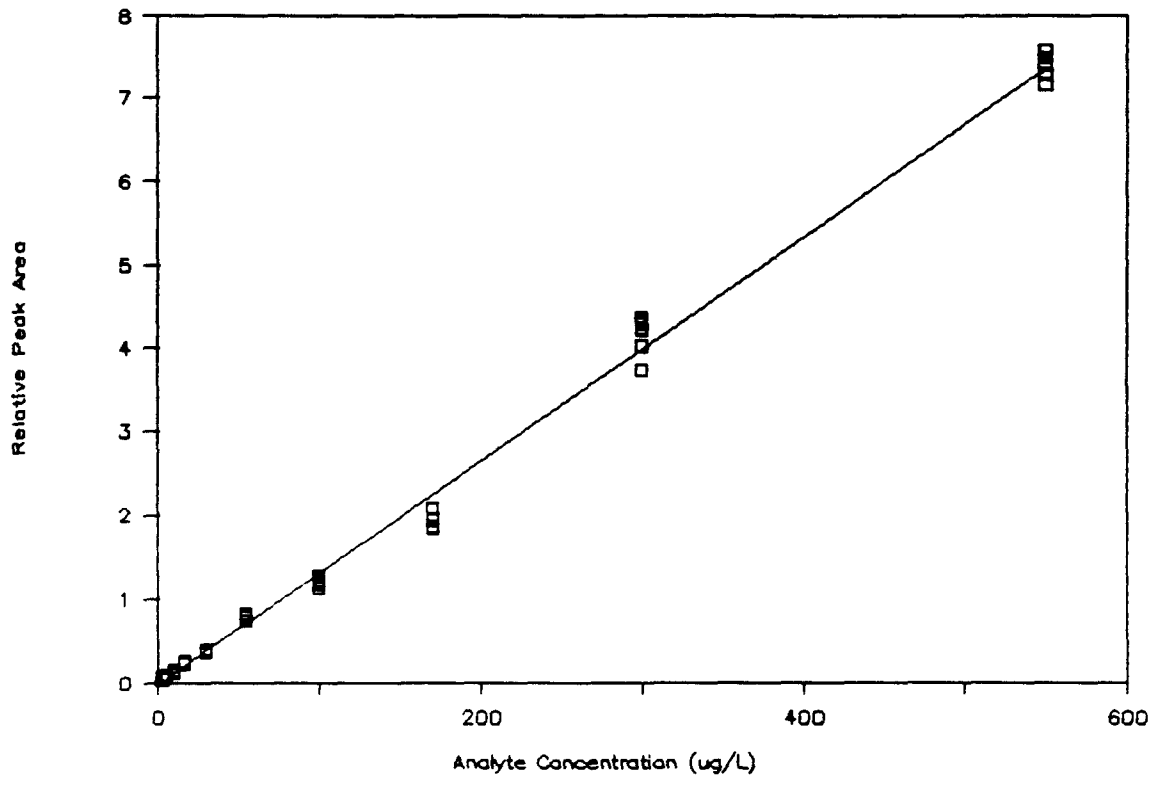
Benzene

Bis-(2-chloroethyl)ether
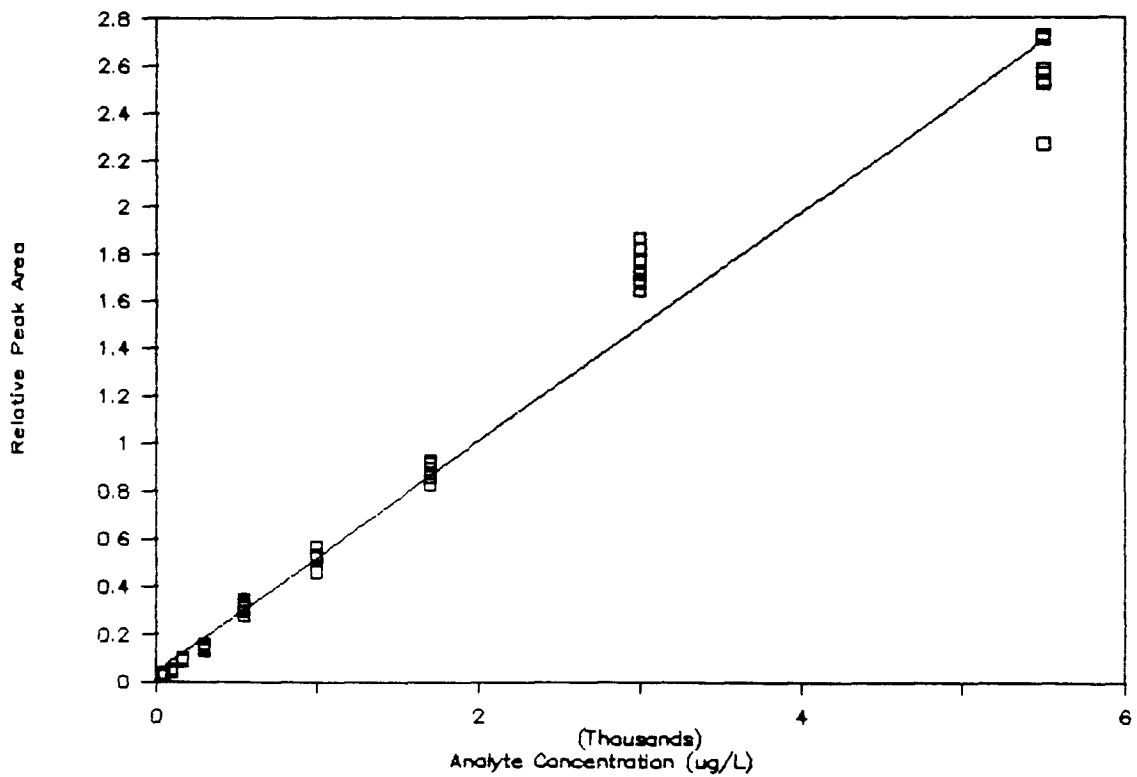
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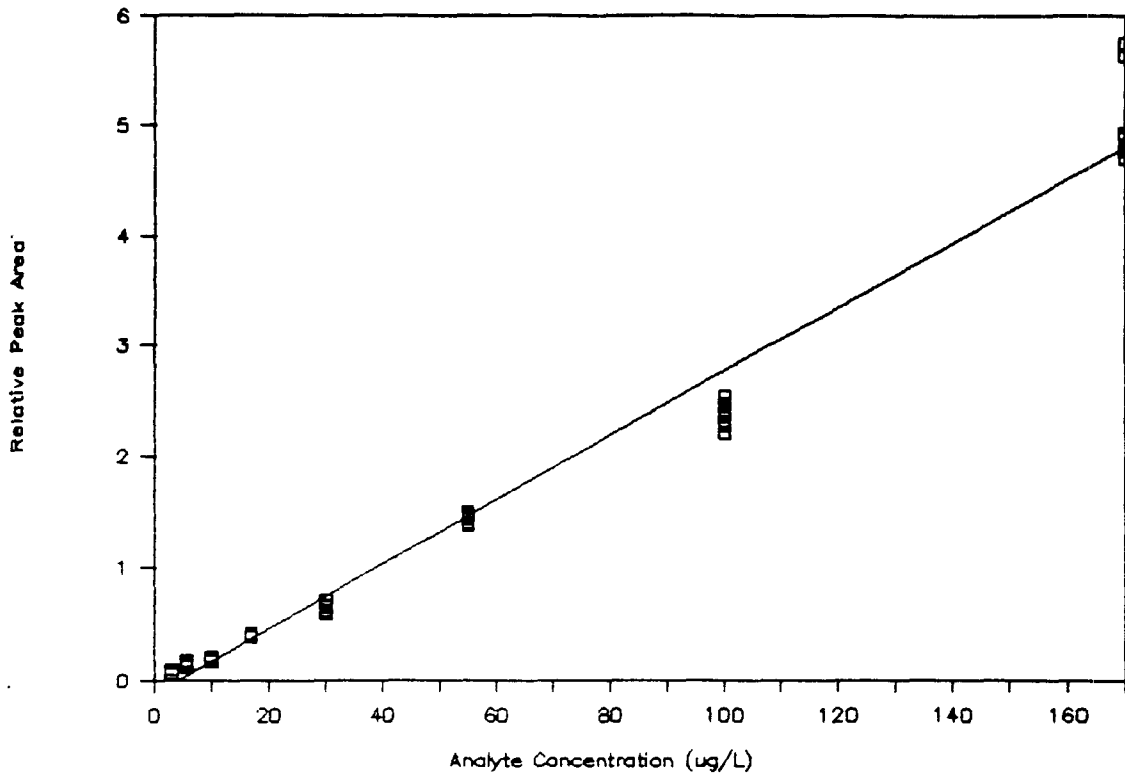
Relative Peak Area vs. Analyte Concentration (ug/L)

Bromodichloromethane

Relative Peak Area vs. Analyte Concentration (ug/L)

Bromomethane

Relative Peak Area vs Analyte Concentration (ug/L)

2-Butanone

Relative Peak Area vs Analyte Concentration (ug/L) (Thousands)
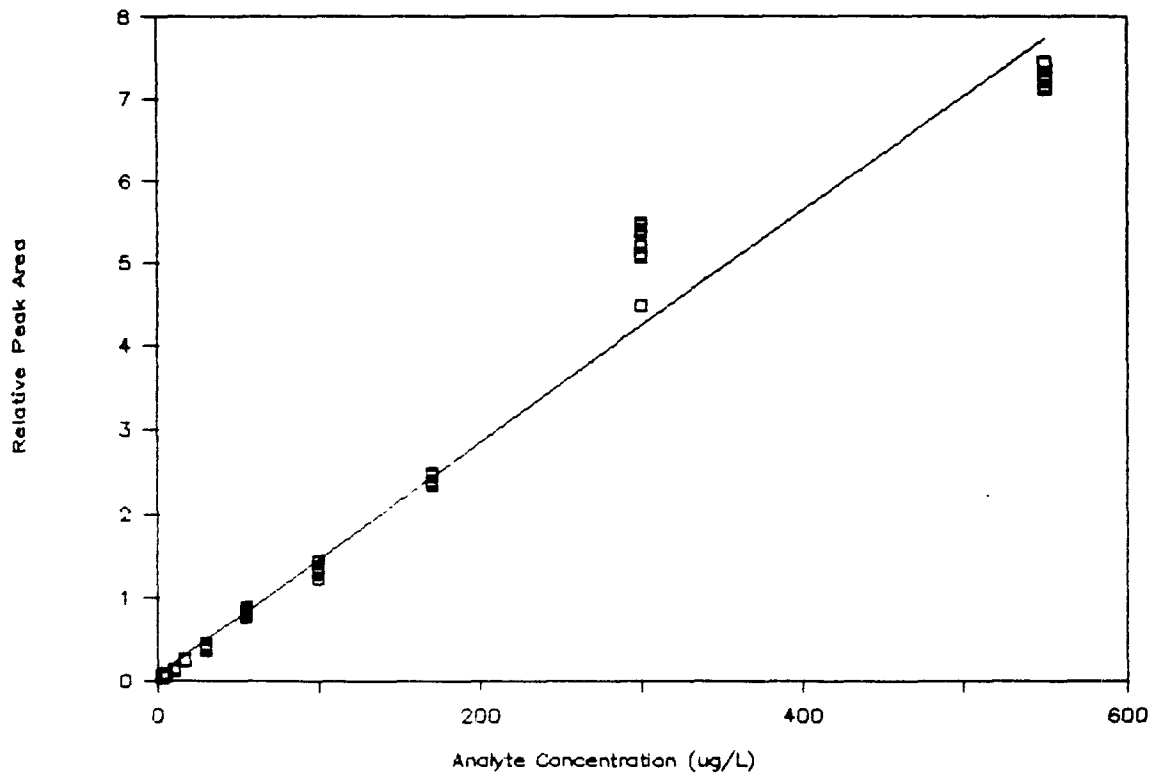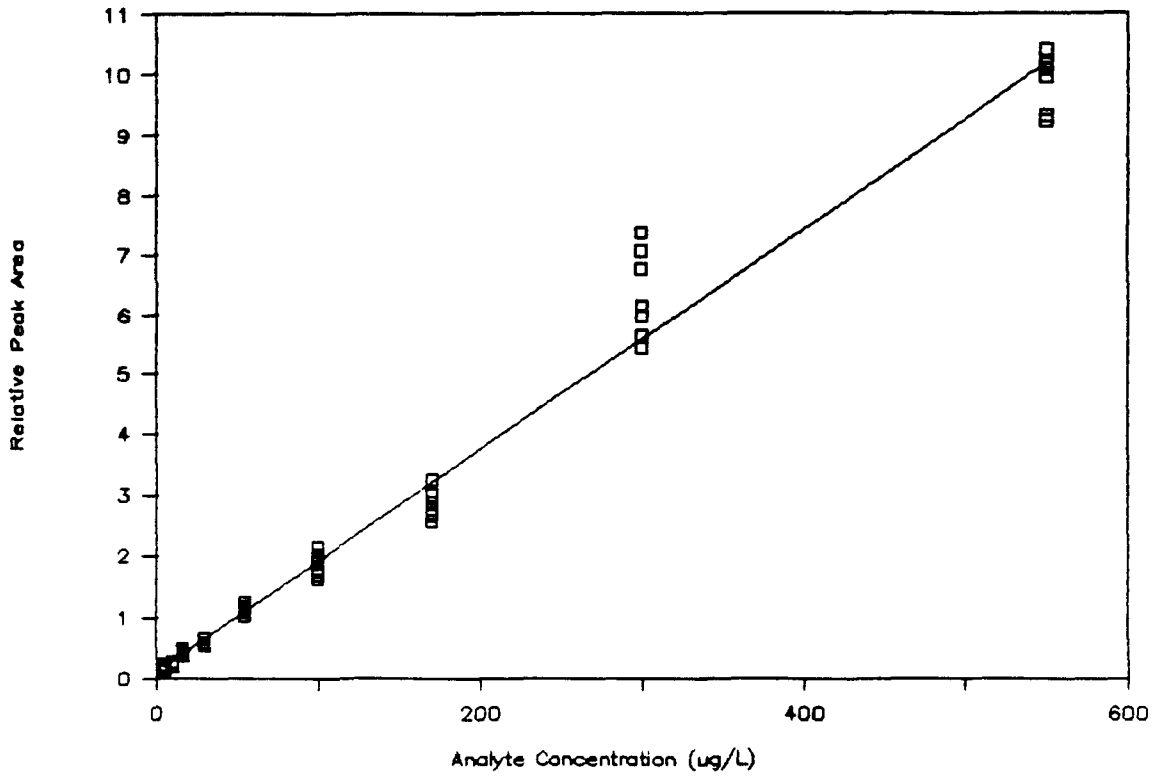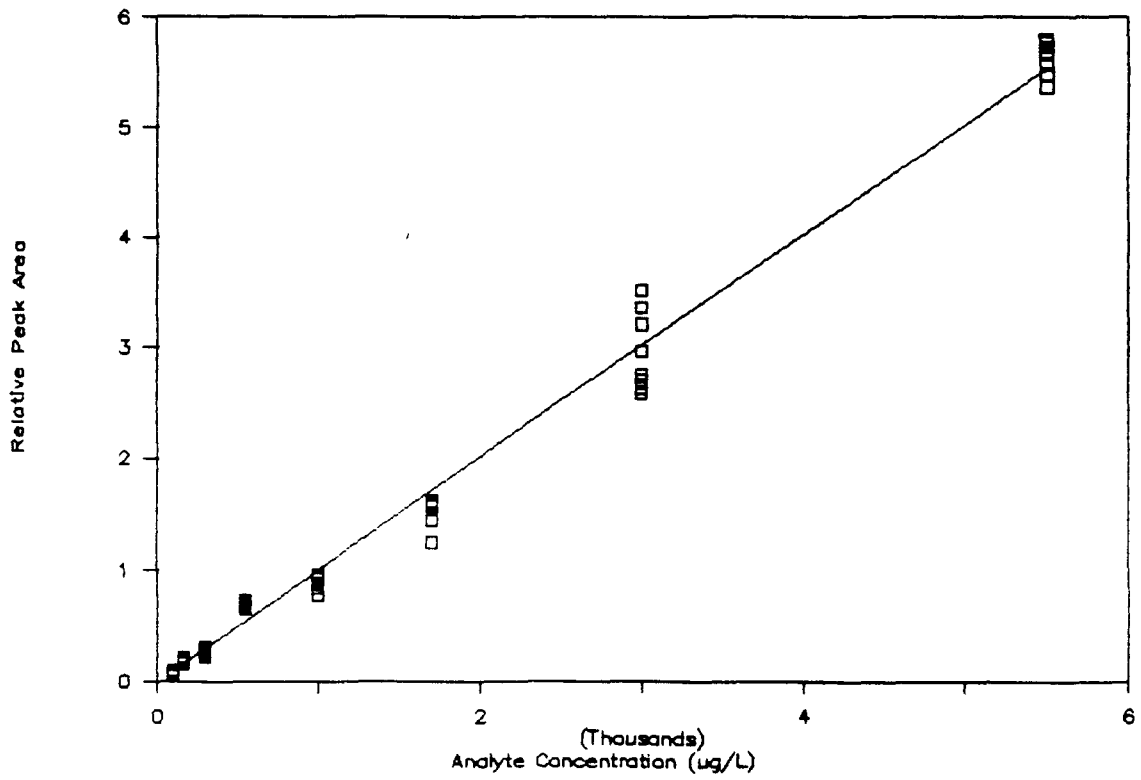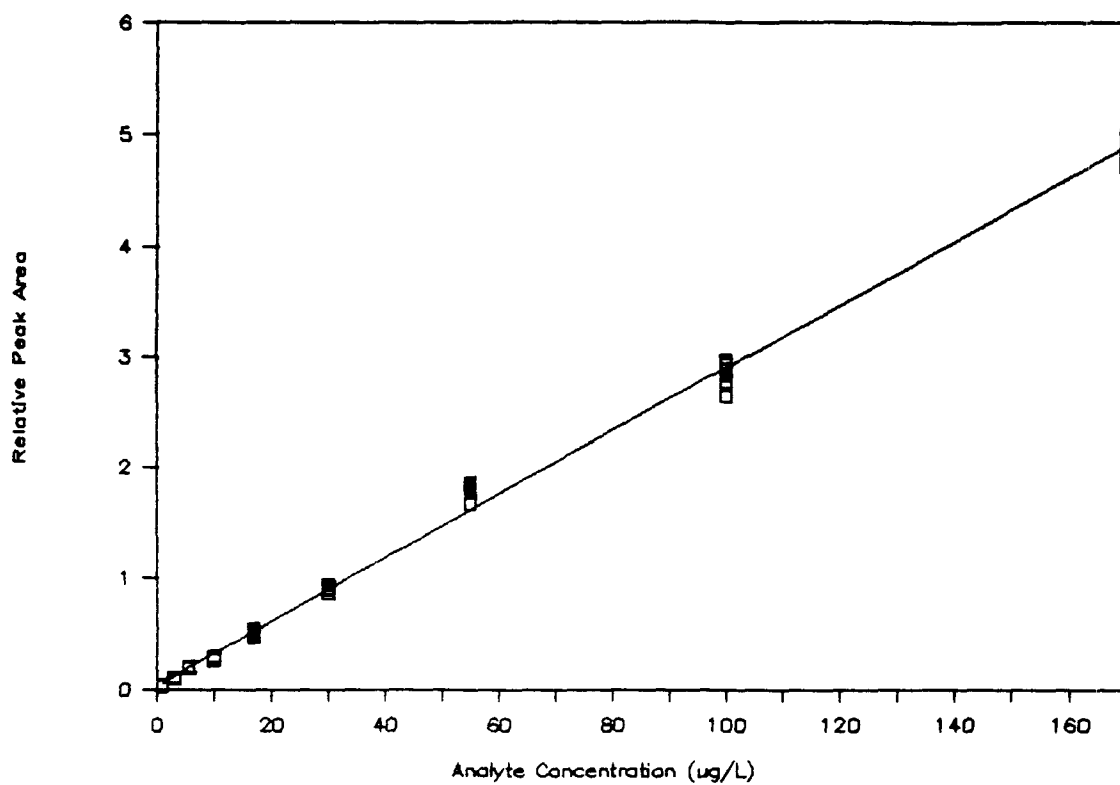
n−Butylbenzene
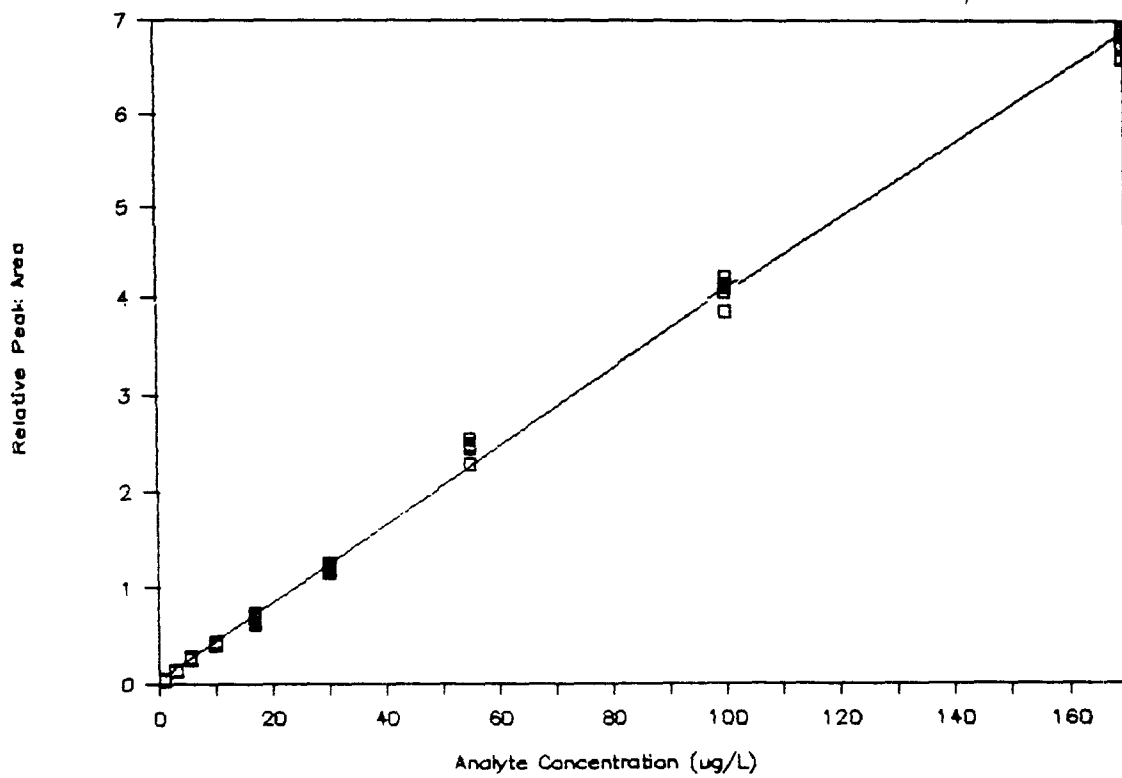
sec−Butylbenzene

tert-Butylbenzene
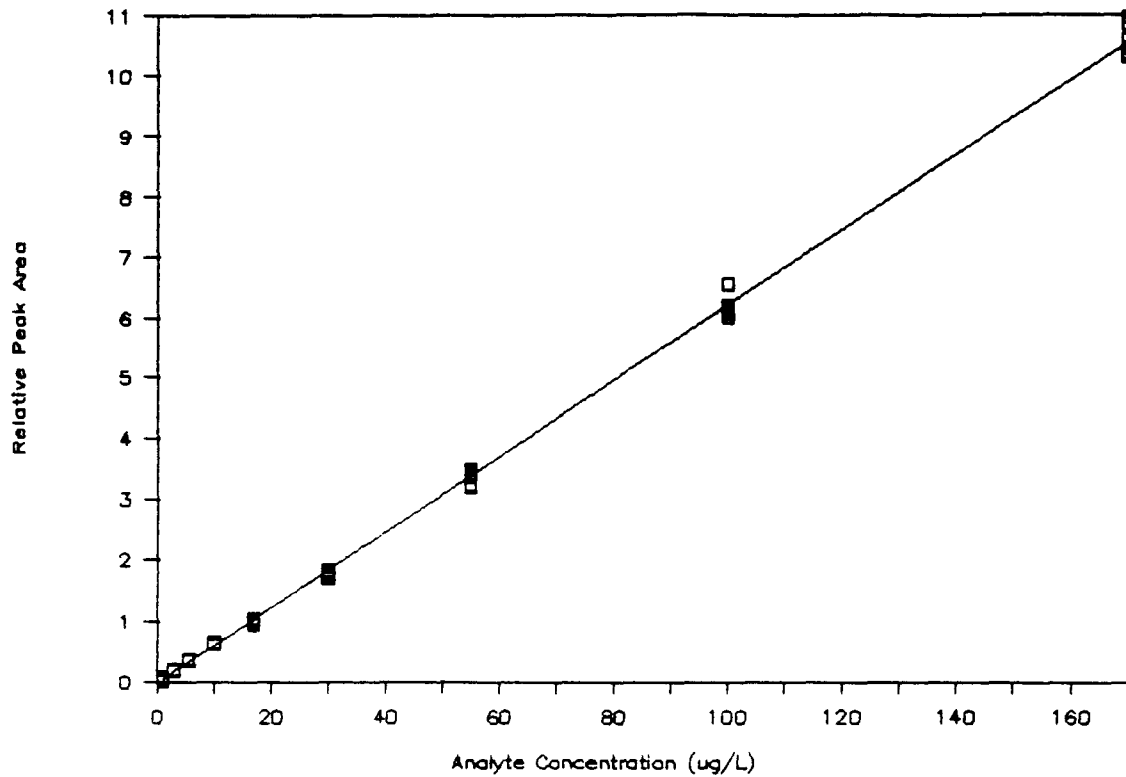
Carbon disulfide
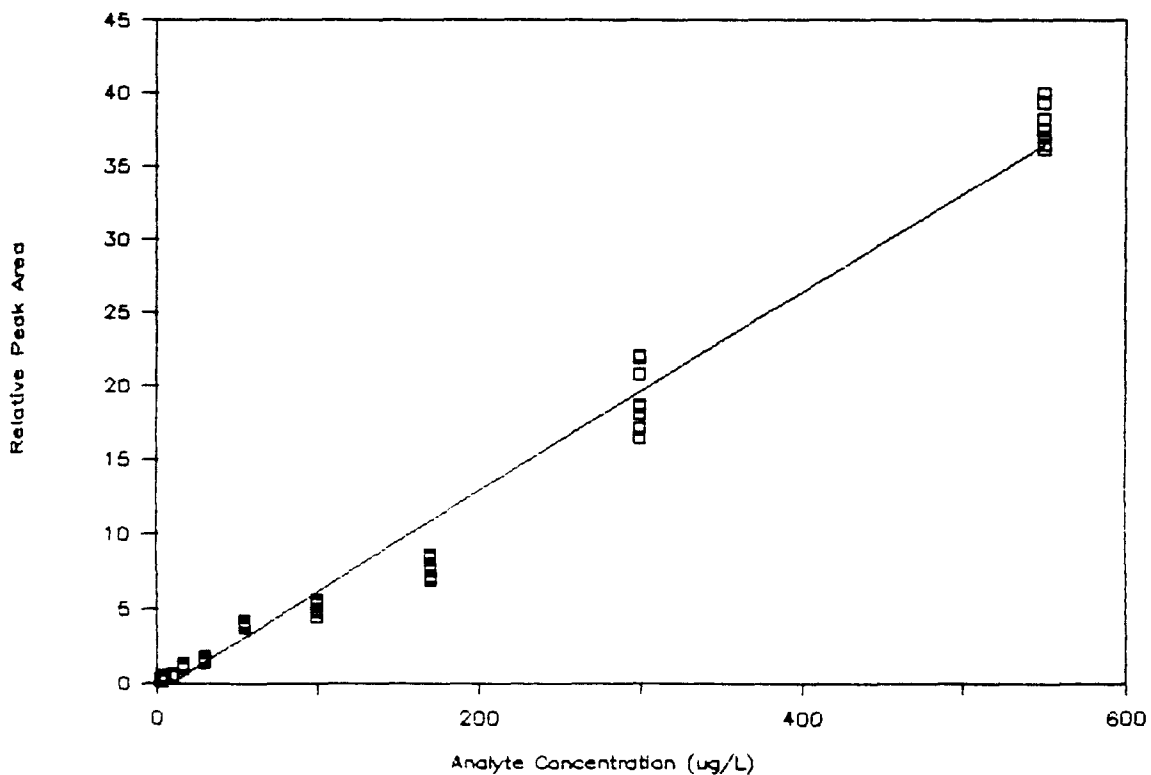
Carbon tetrachloride

Chlorobenzene

A-8
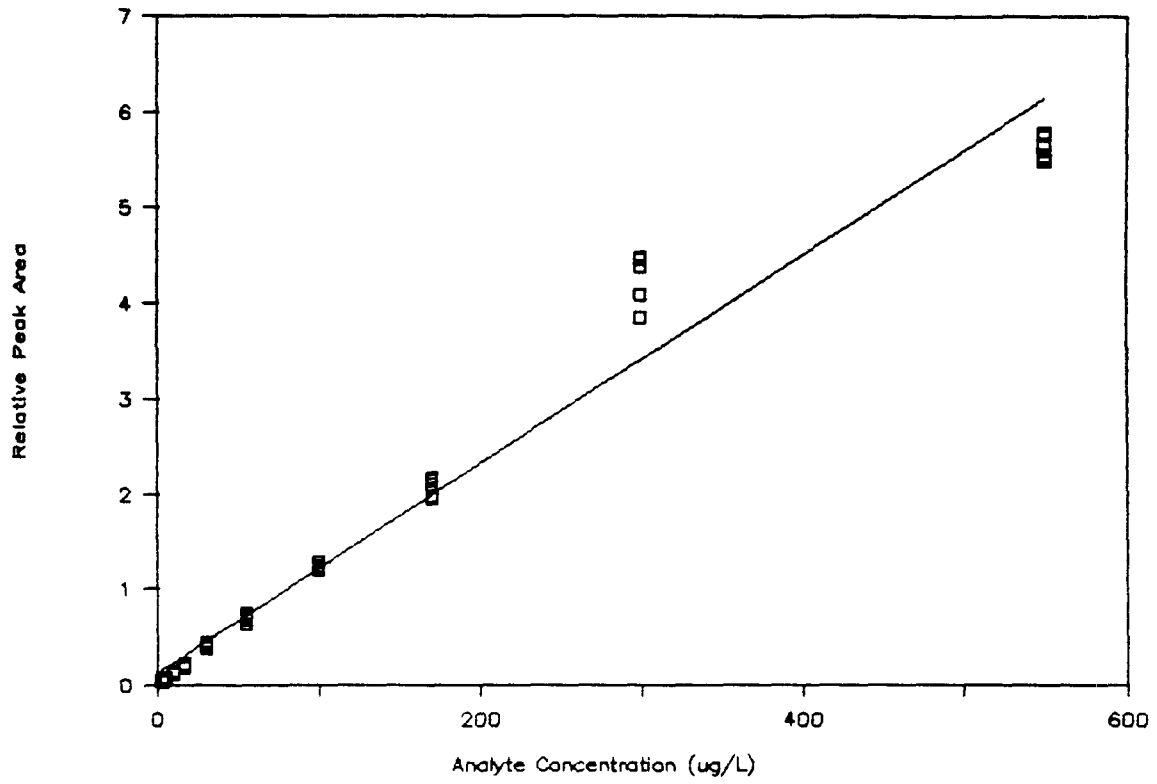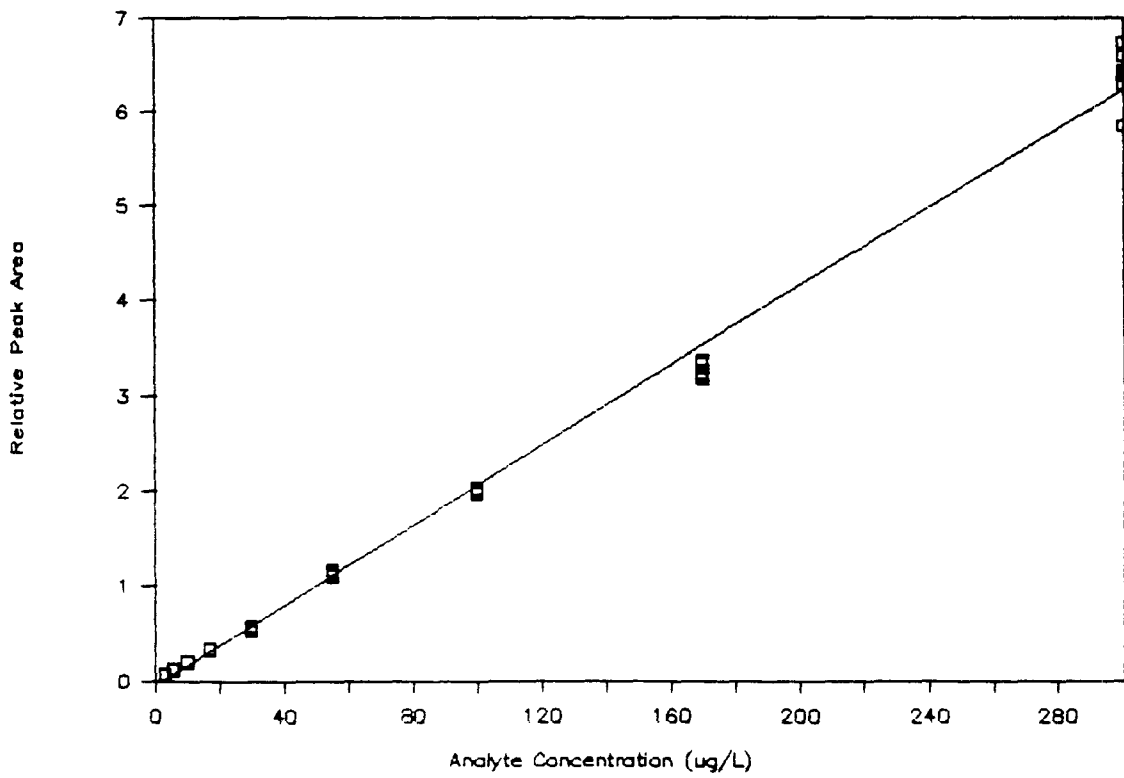
2-Chloro-1,3-butadiene

Chlorodibromomethane

A-9
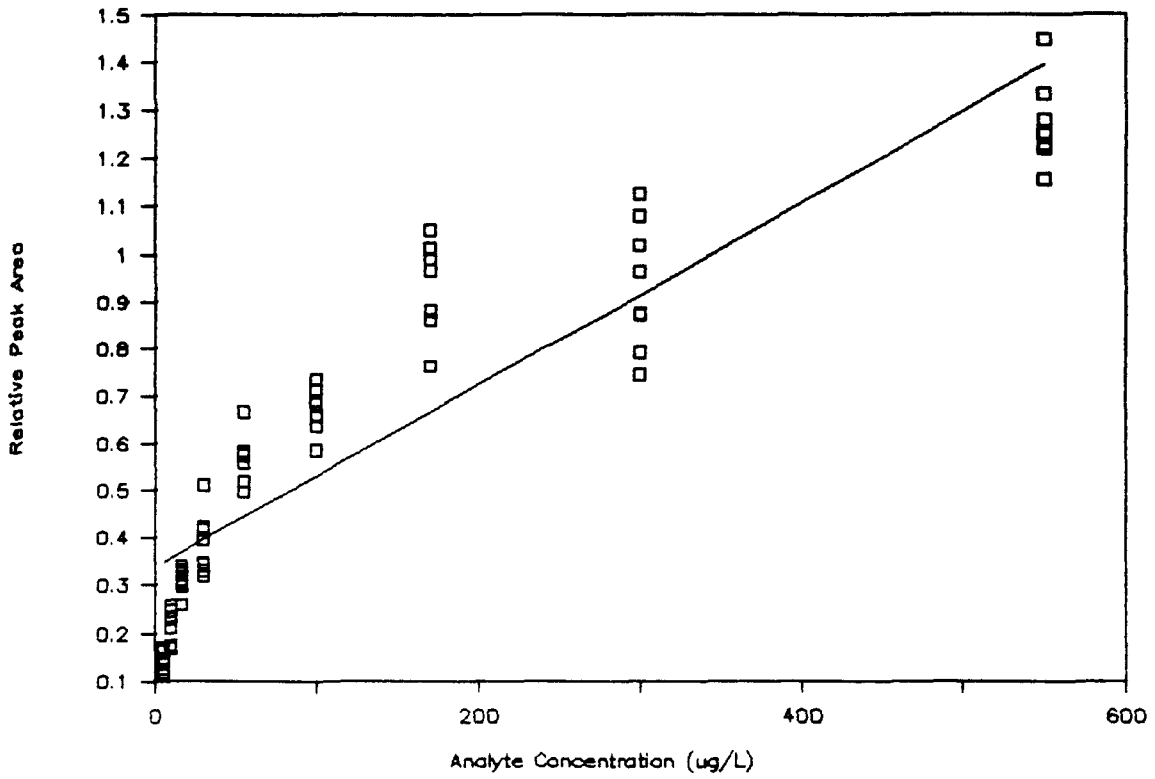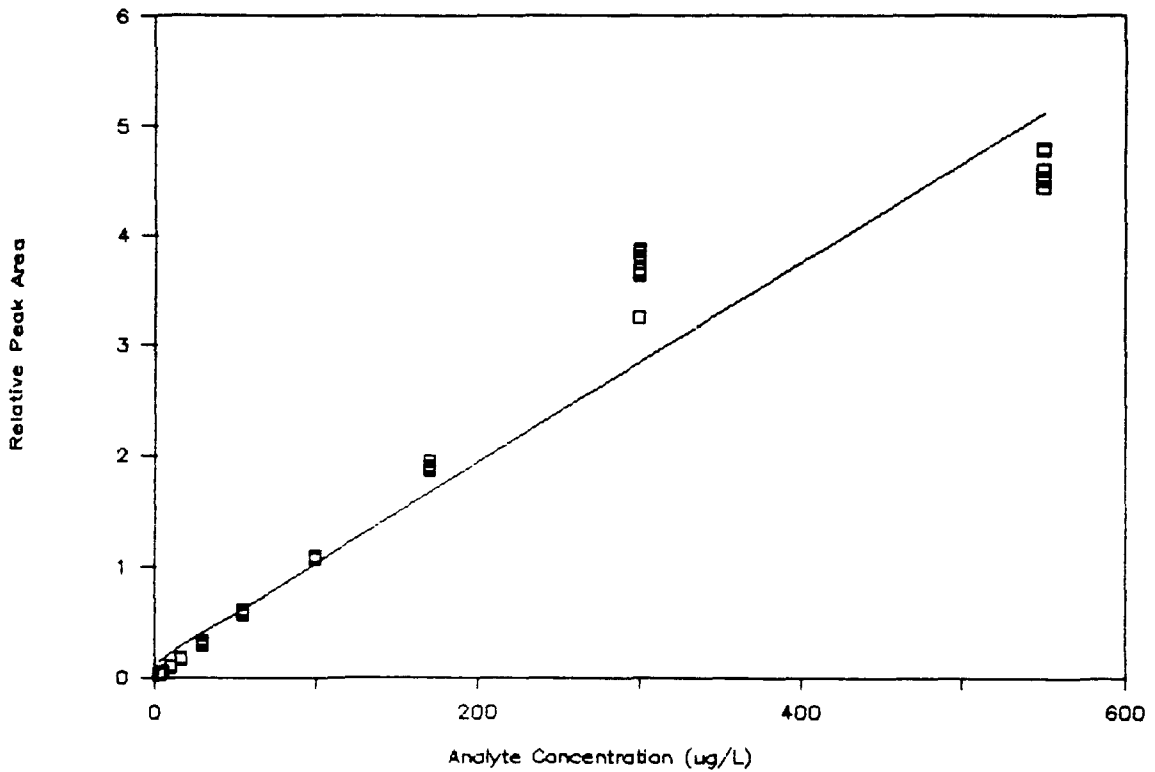
Chloroethane

2-Chloroethyl ethyl ether

A-10
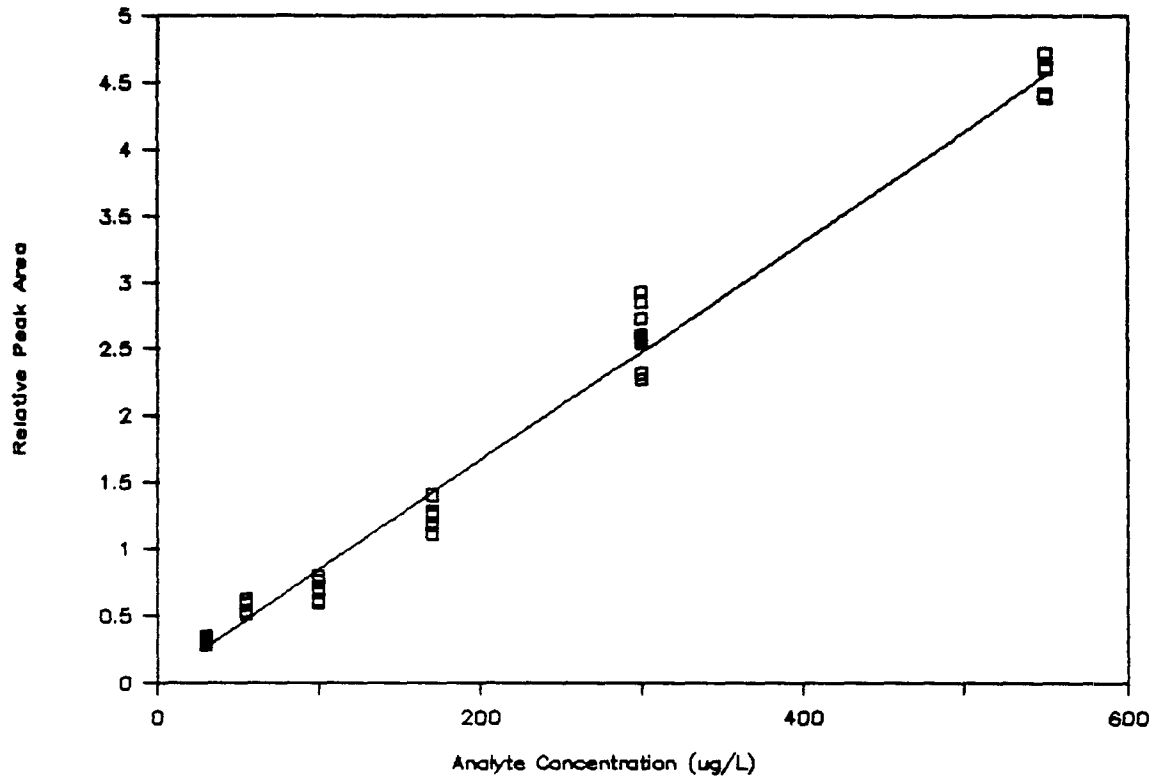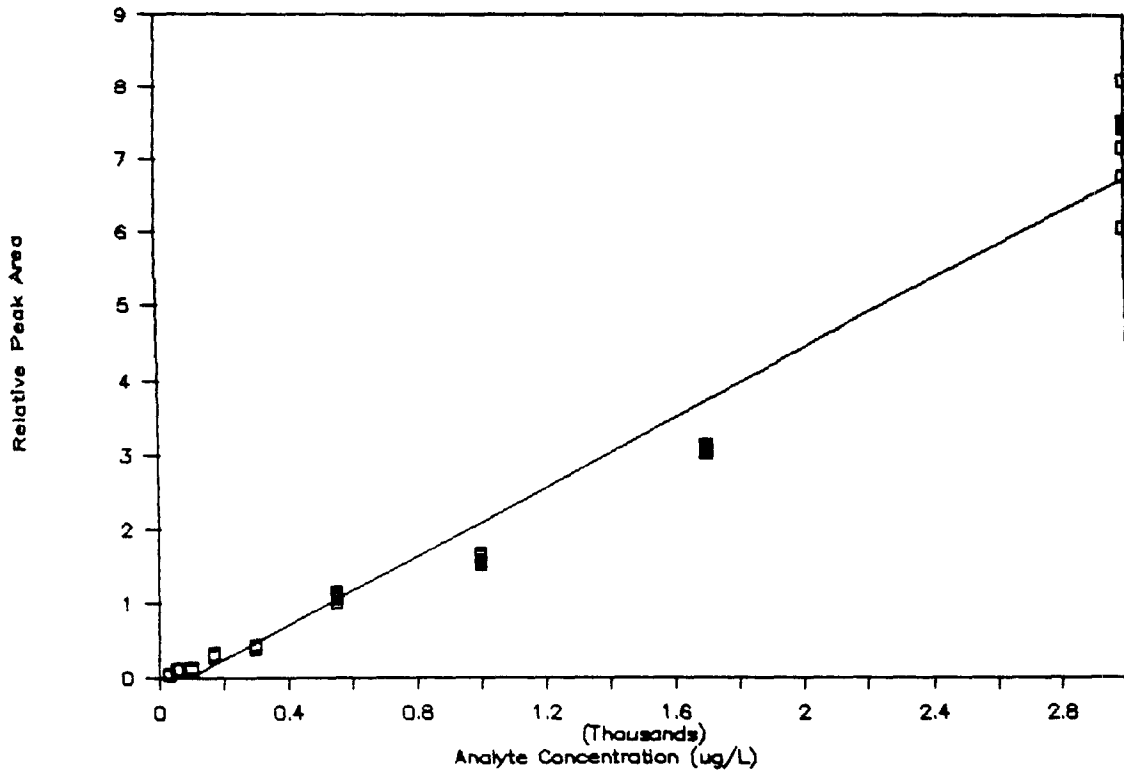
Chloroform
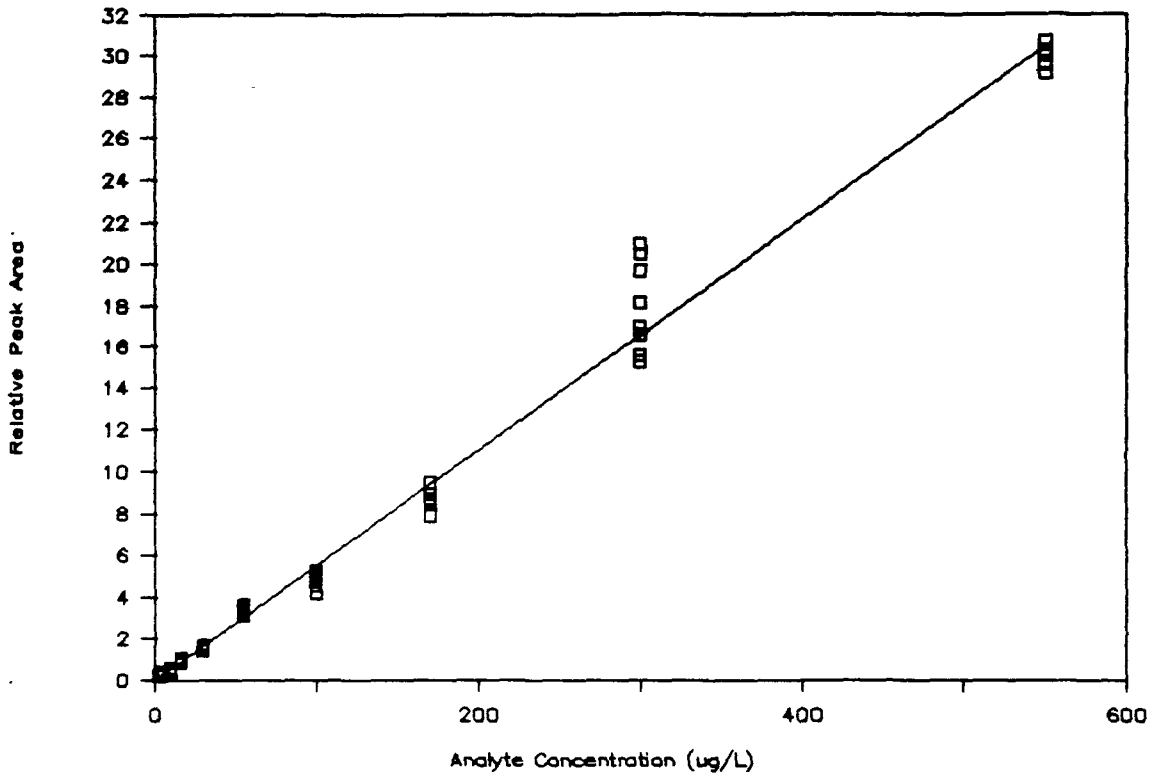
1-Chlorohexane
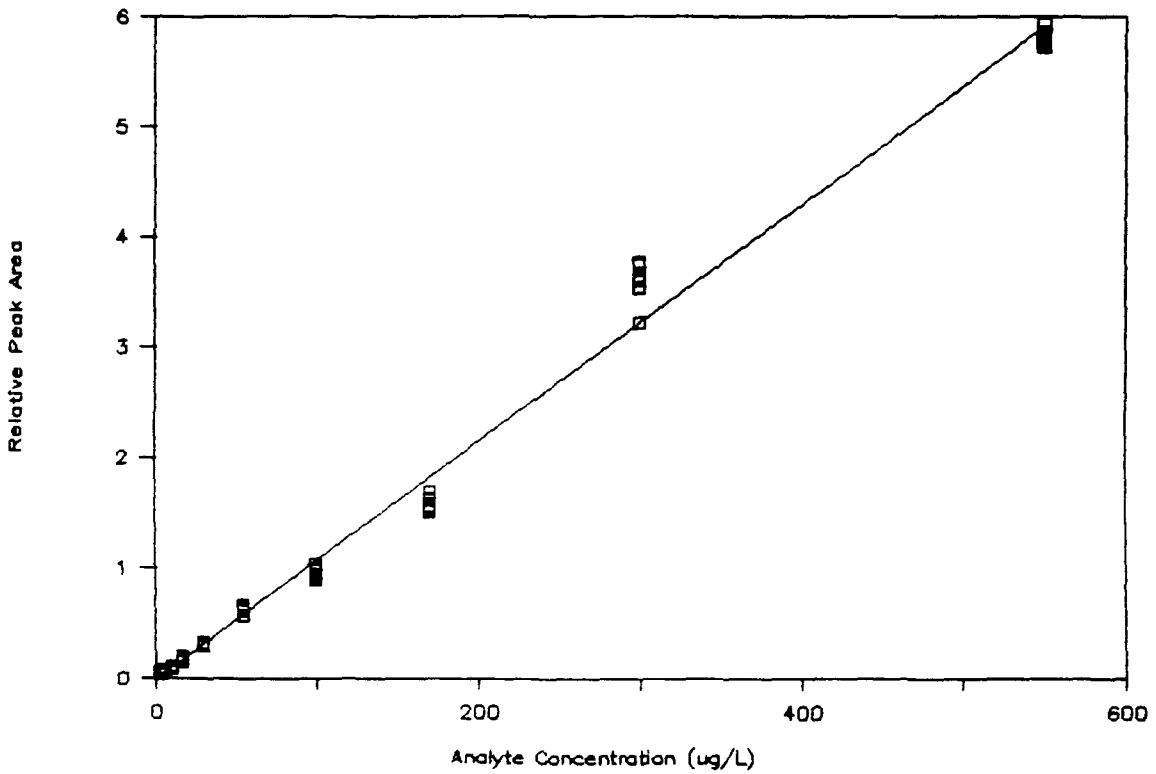
Chloromethane
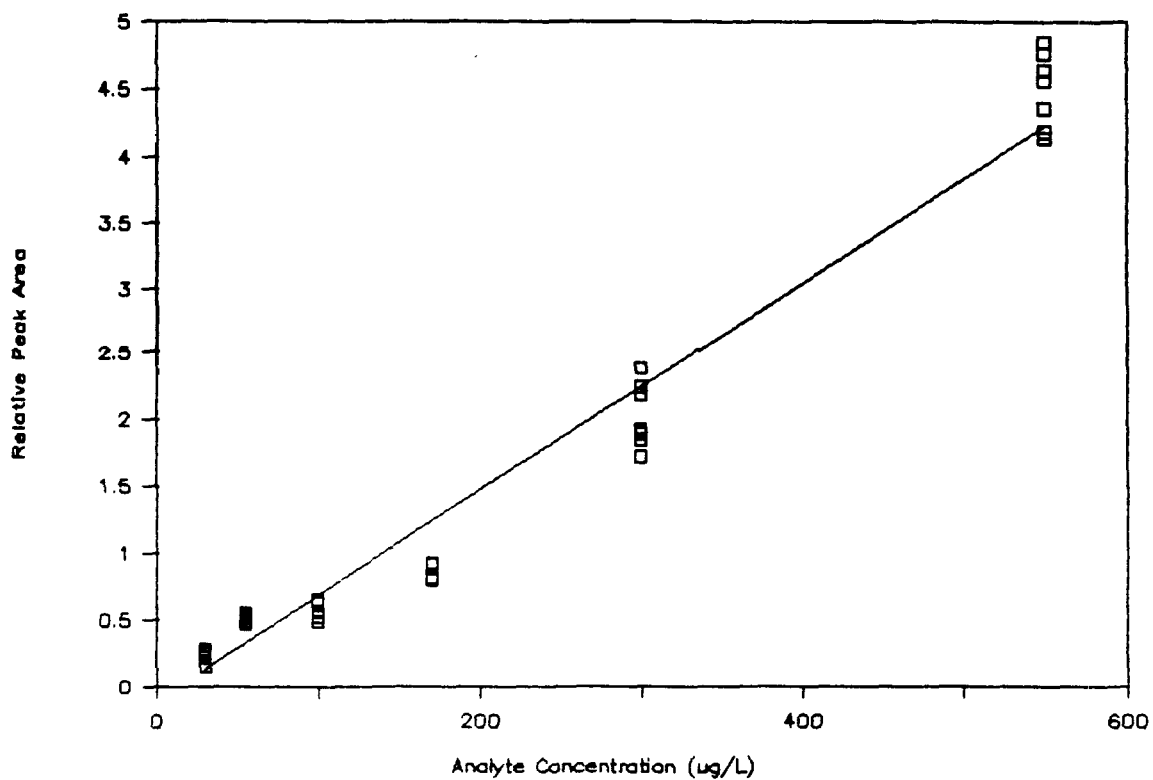
2-Chlorotoluene
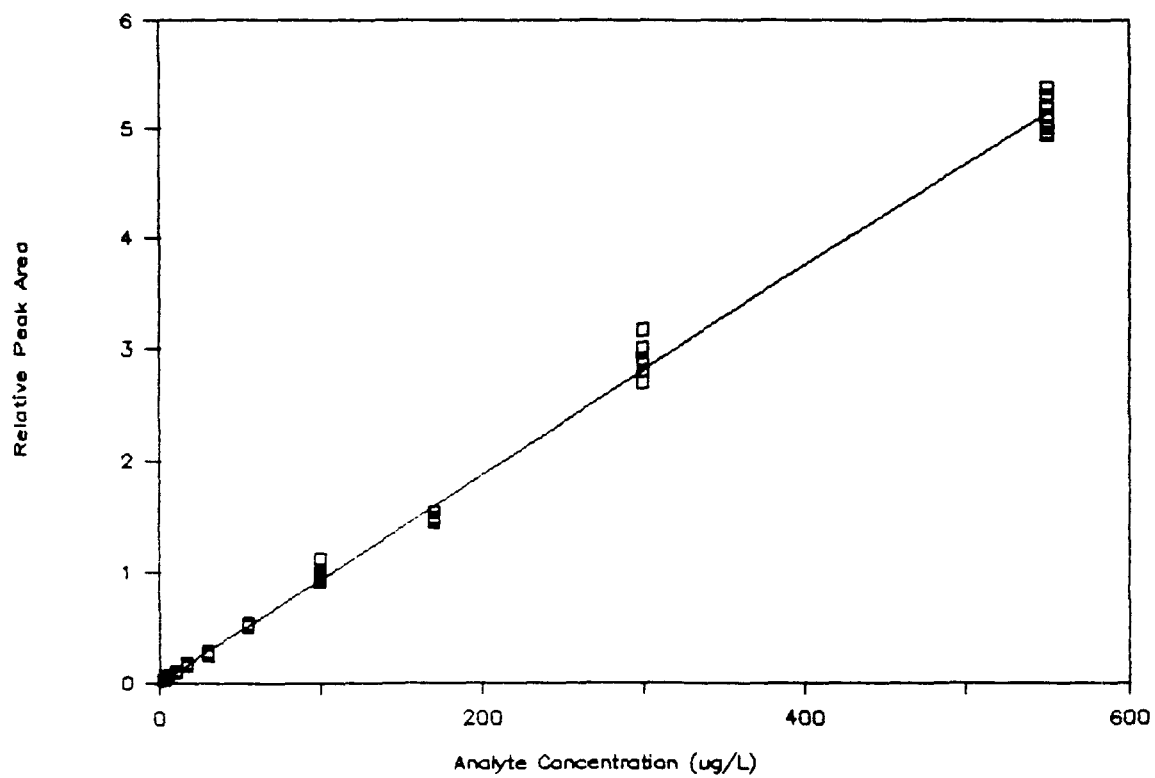
4–Chlorotoluene
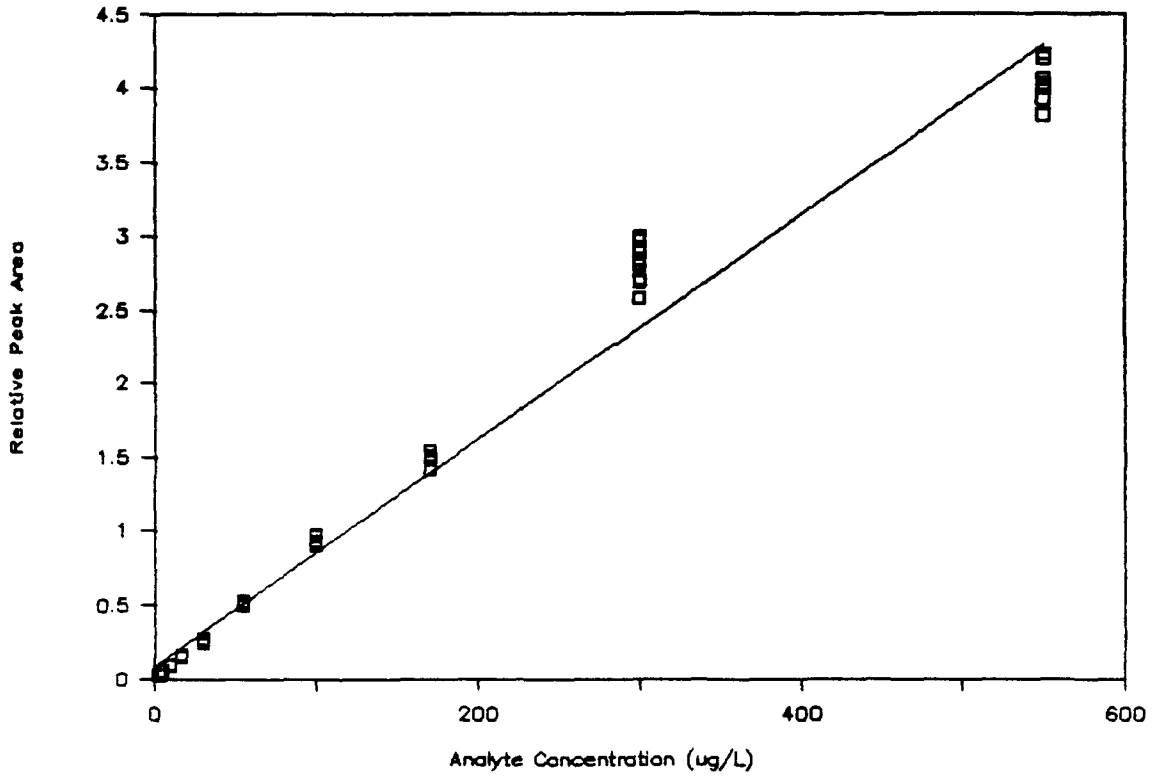
1,2–Dibromo–3–chloropropane
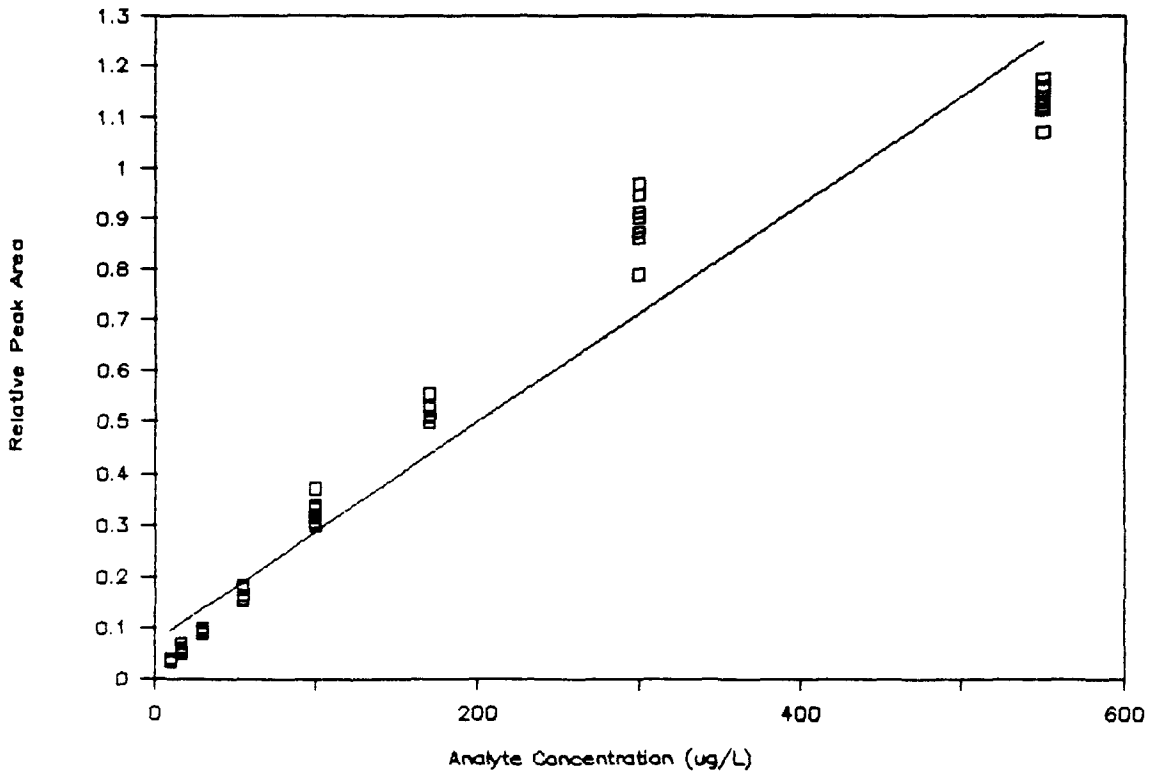
1,2-Dibromoethane

Dibromomethane

A-14
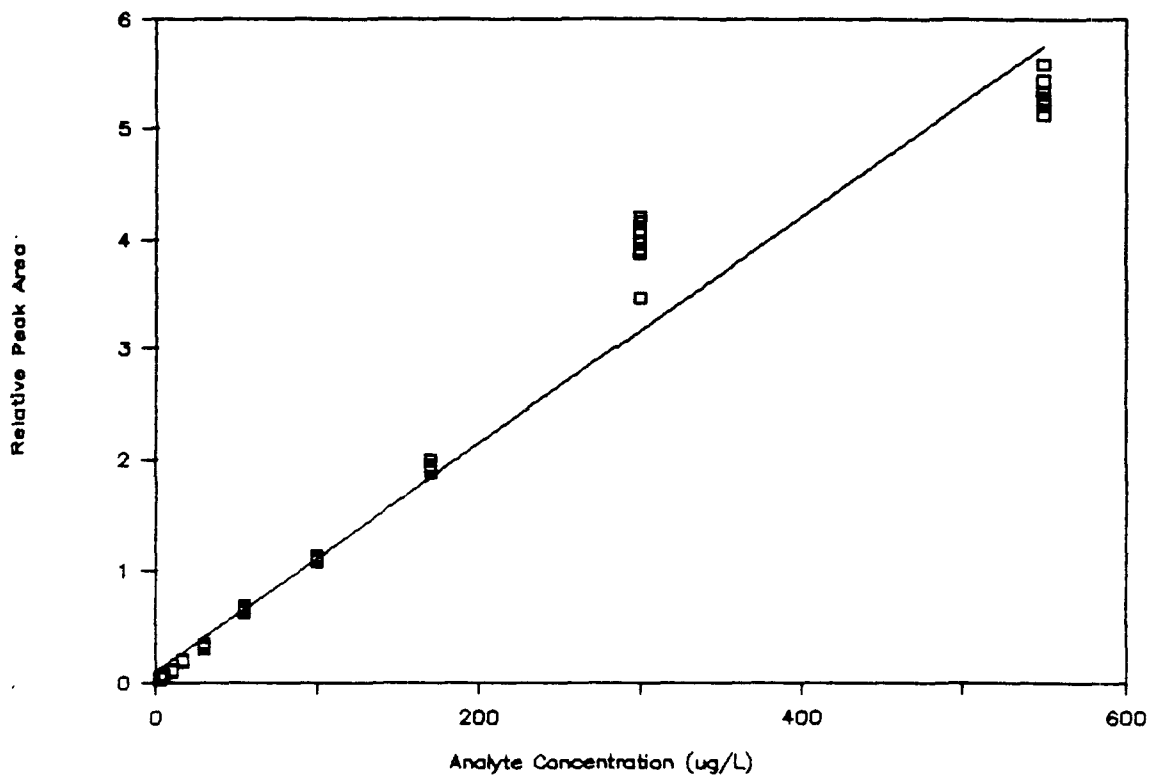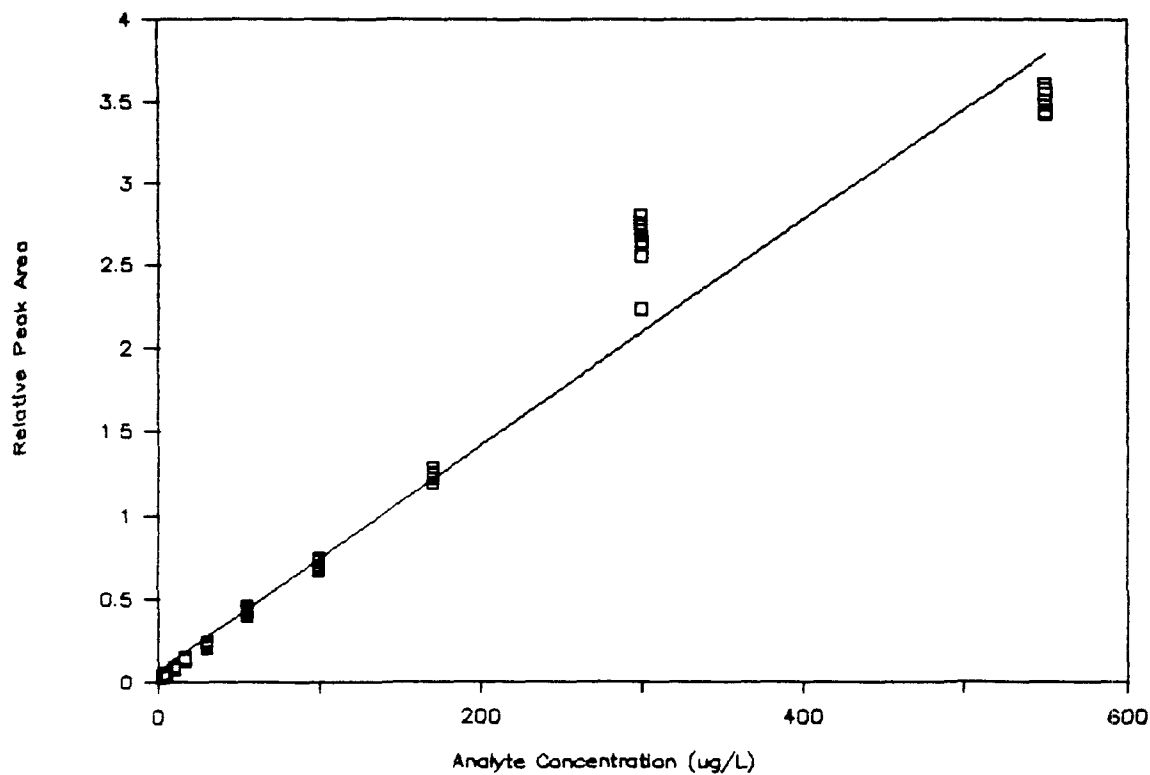
1,2–Dichlorobenzene
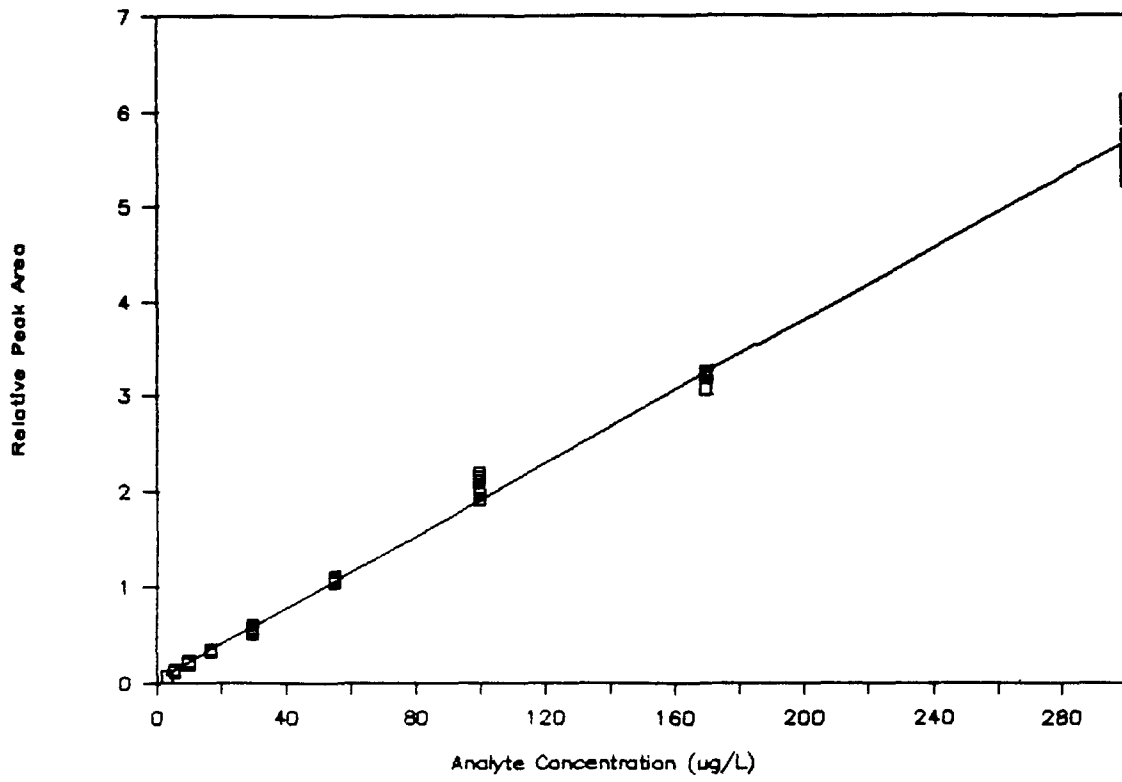
1,3–Dichlorobenzene
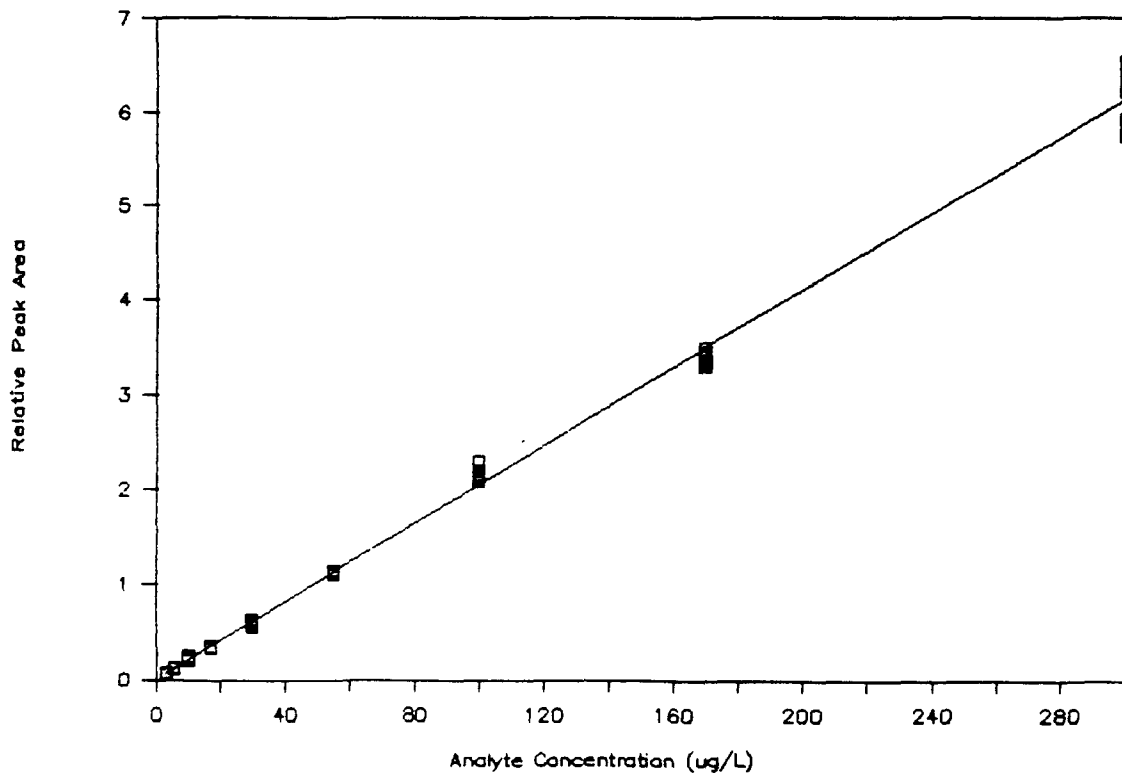
1,4-Dichlorobenzene
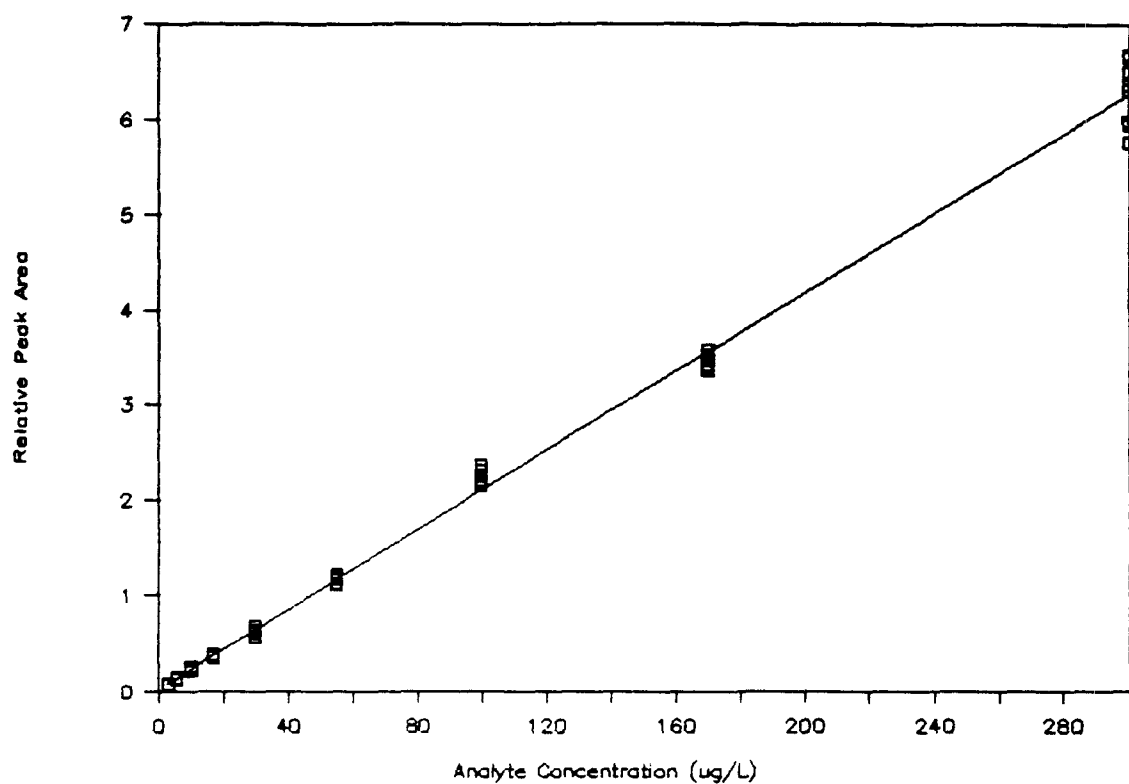
trans-1,4-Dichloro-2-butene
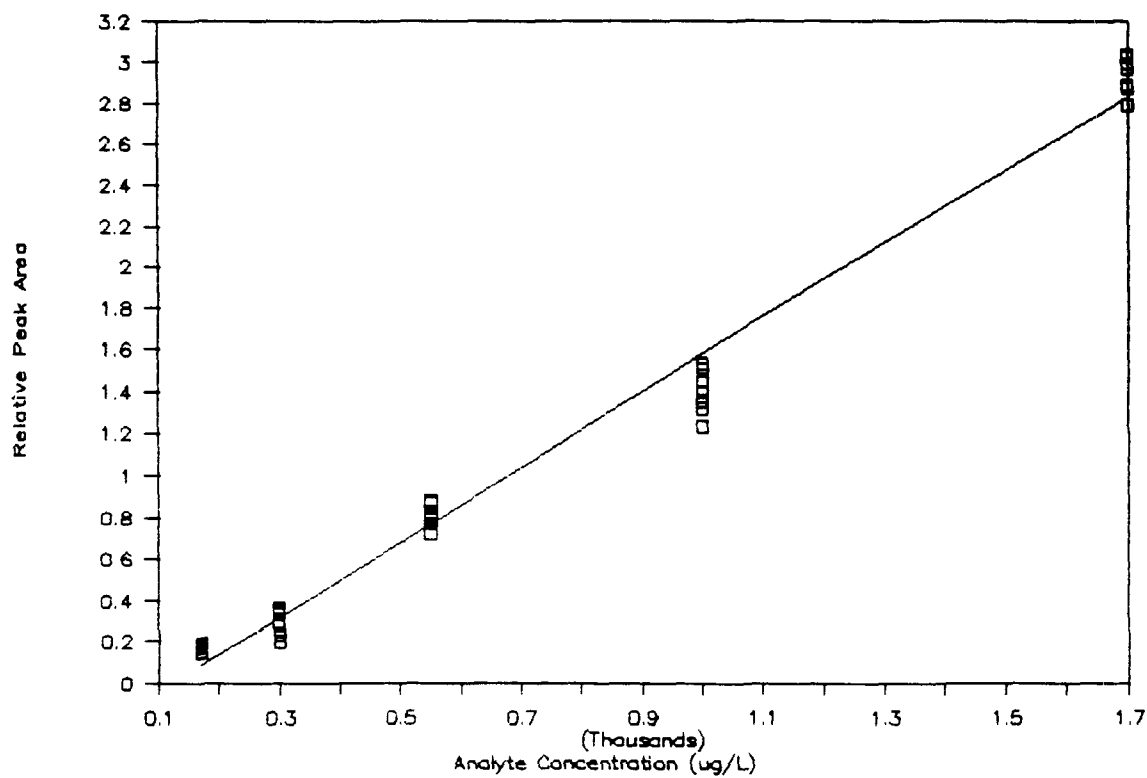
Dichlorodifluoromethane
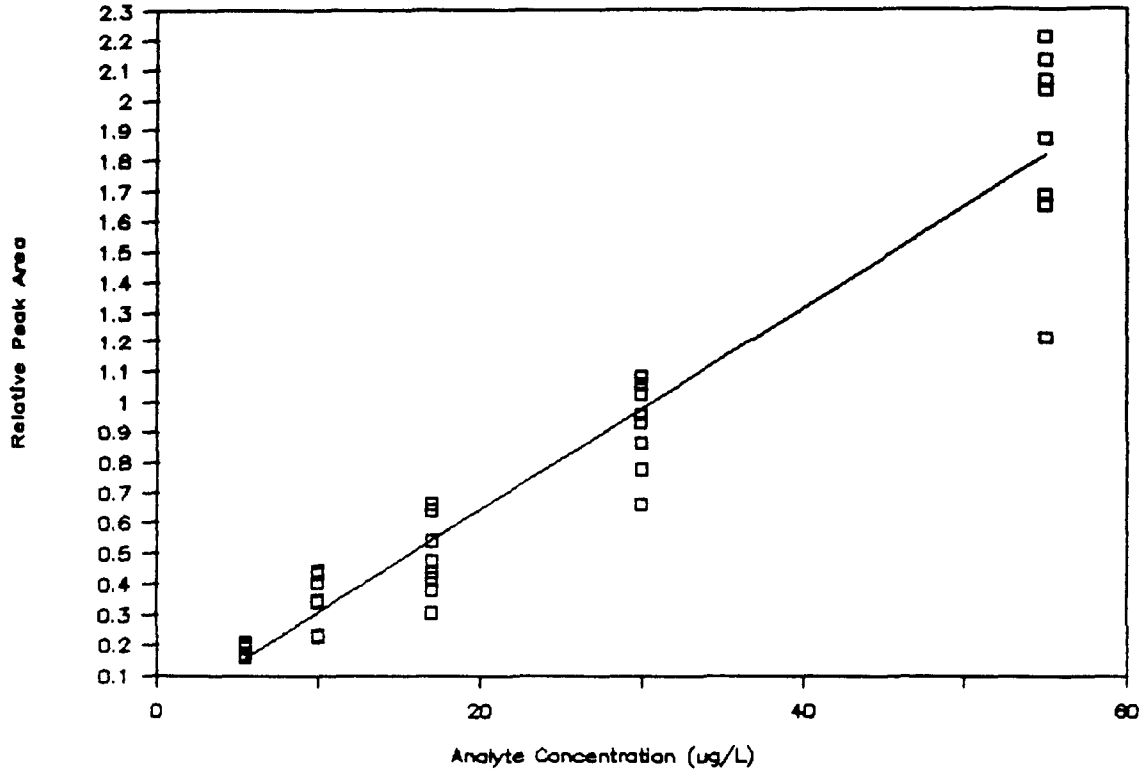
1,1-Dichloroethane
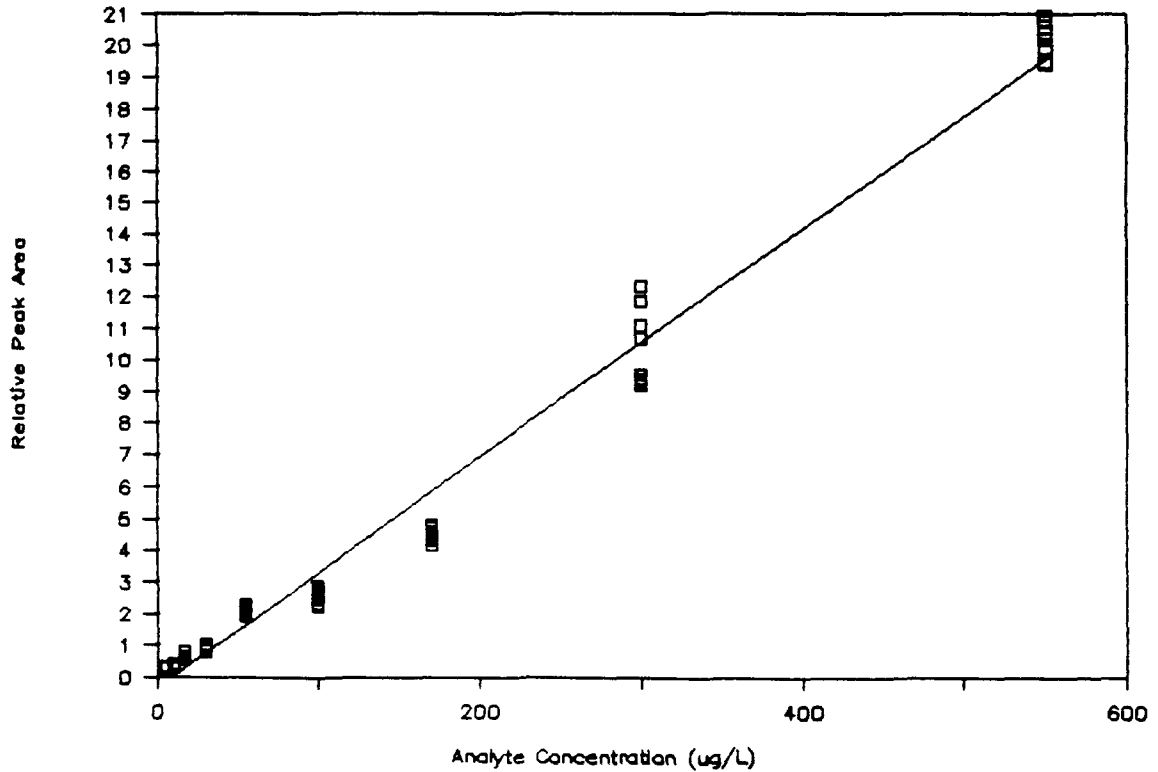
1,2-Dichloroethane
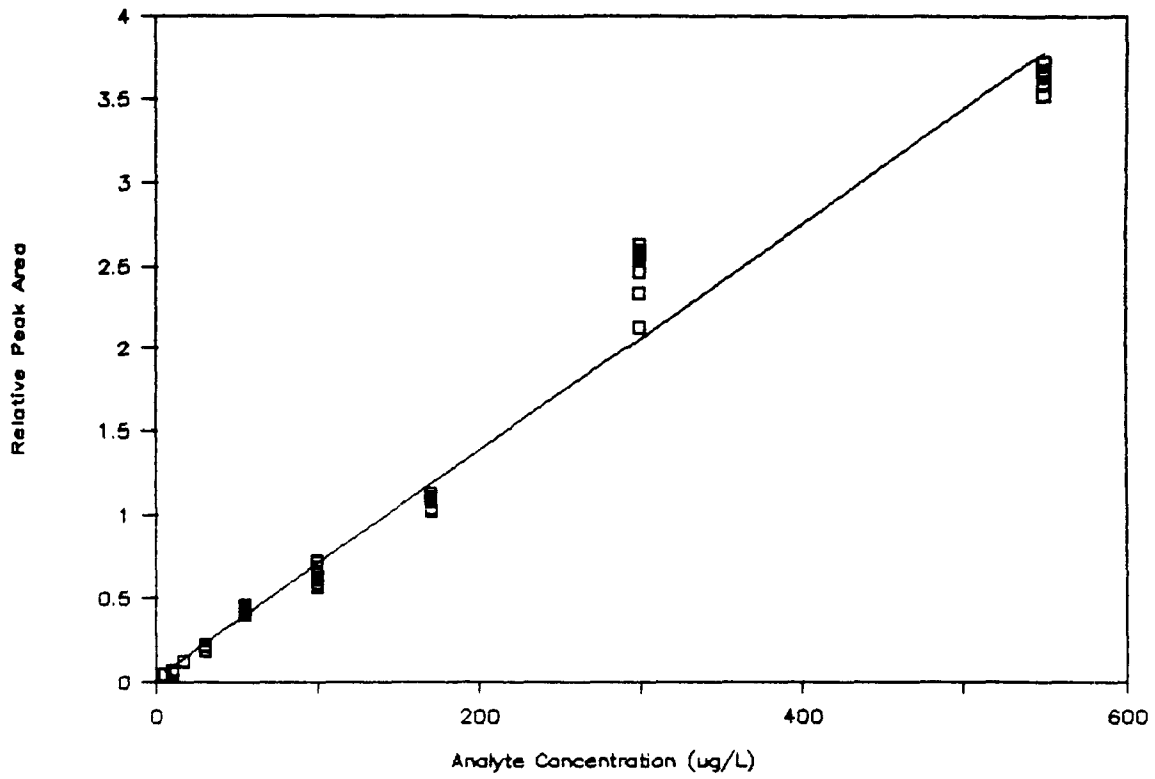
1,1-Dichloroethene

cis−1,2−Dichloroethene

Relative Peak Area vs. Analyte Concentration (ug/L)

trans−1,2−Dichloroethene

Relative Peak Area vs. Analyte Concentration (ug/L)

A-19
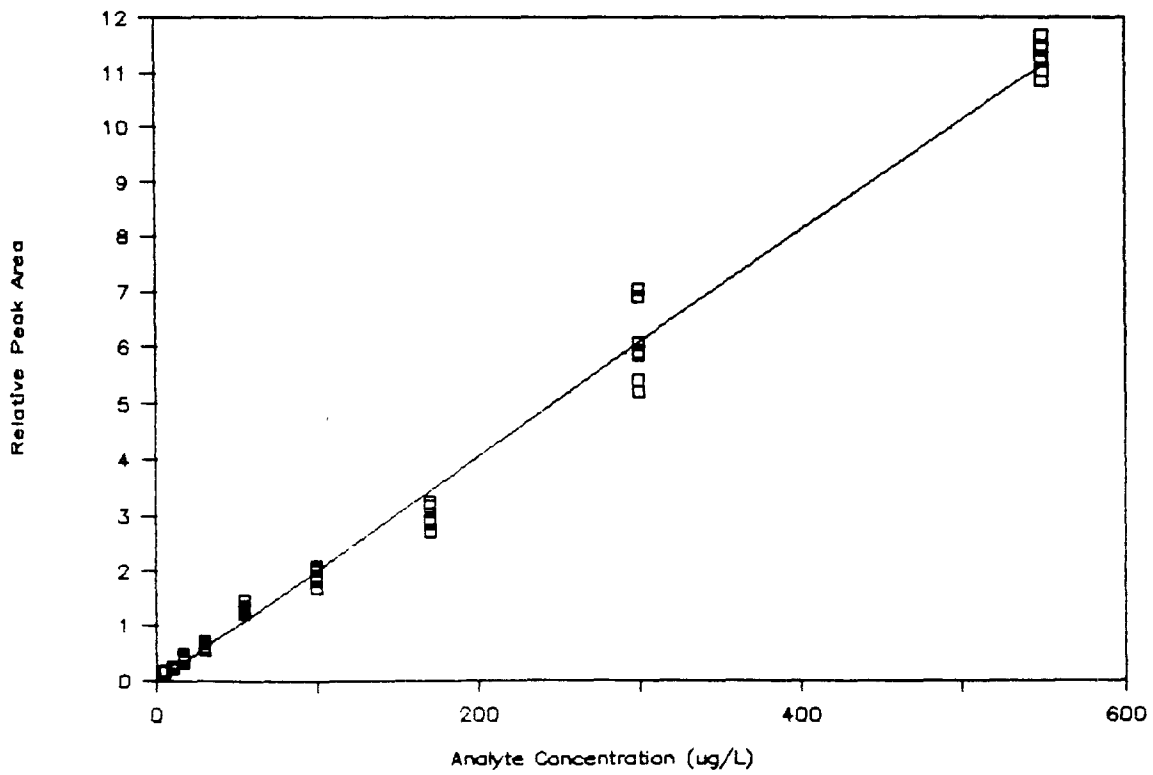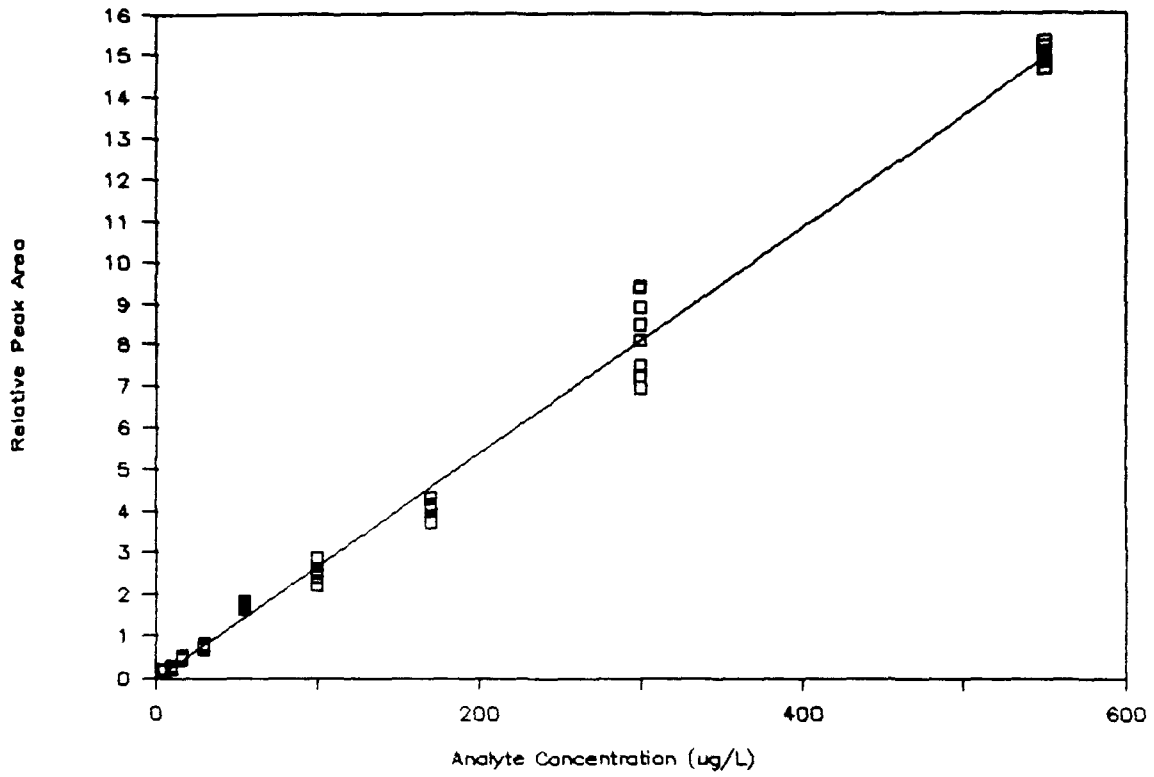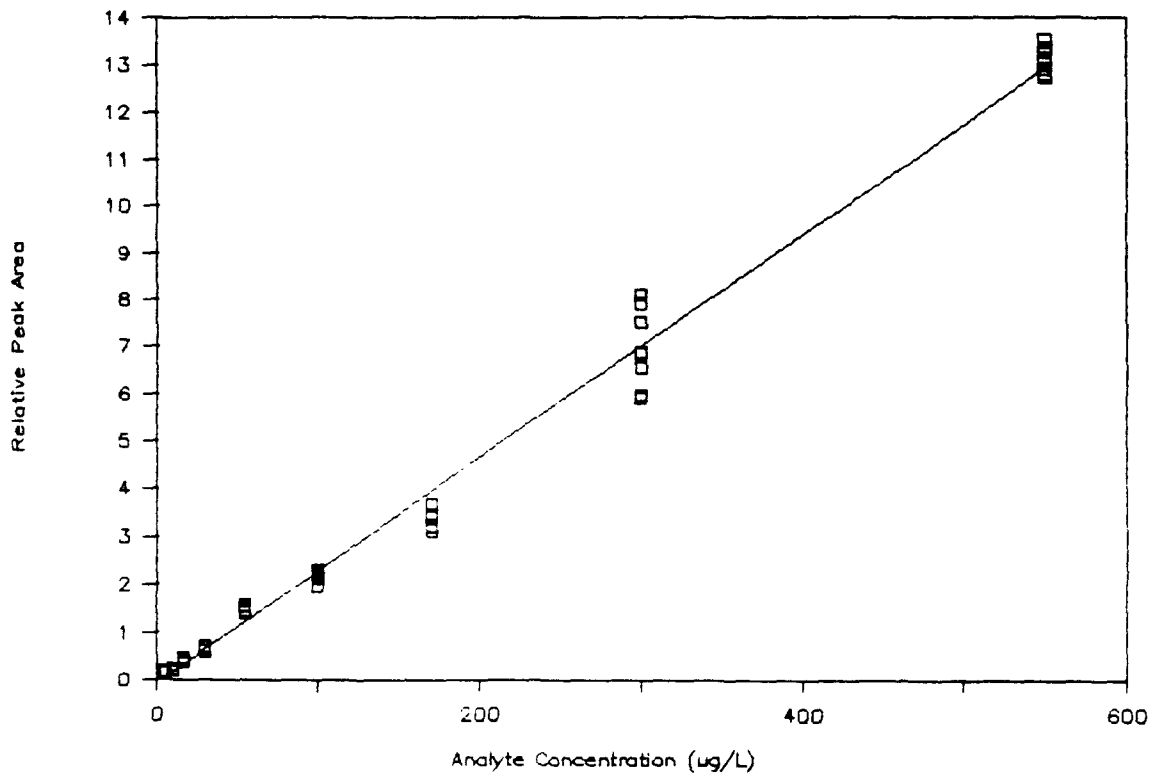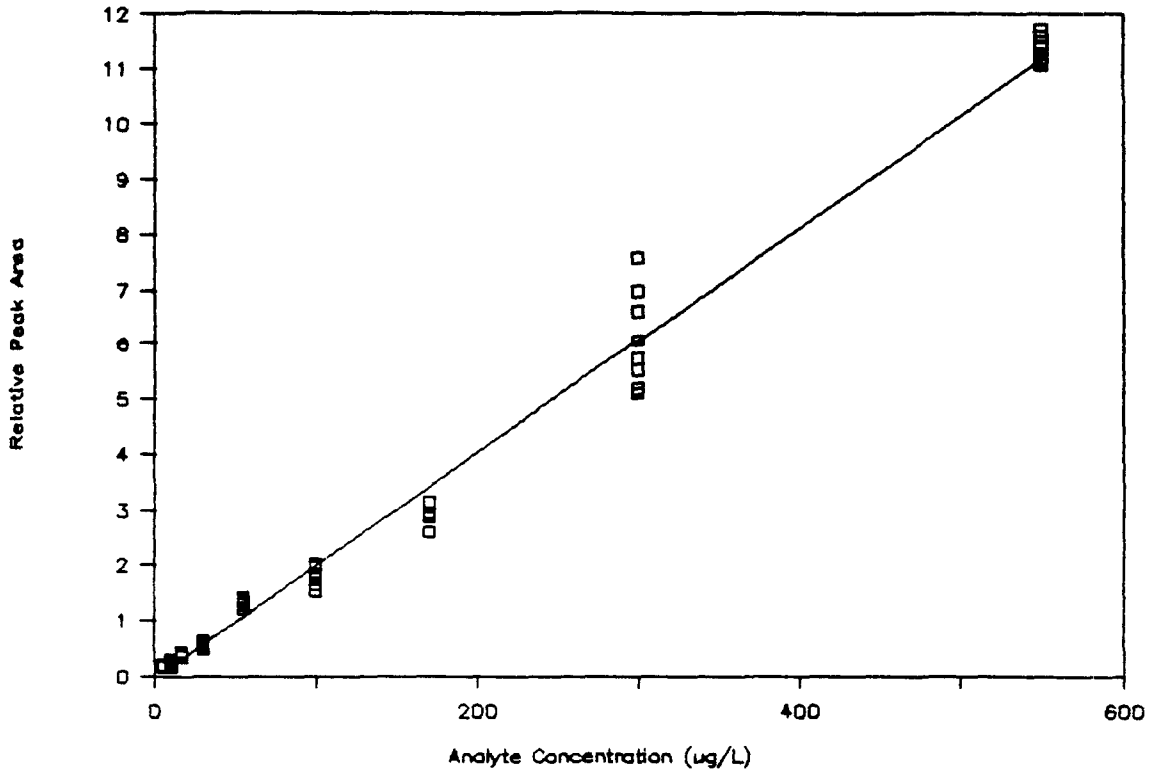
Dichloromethane

1,2-Dichloropropane
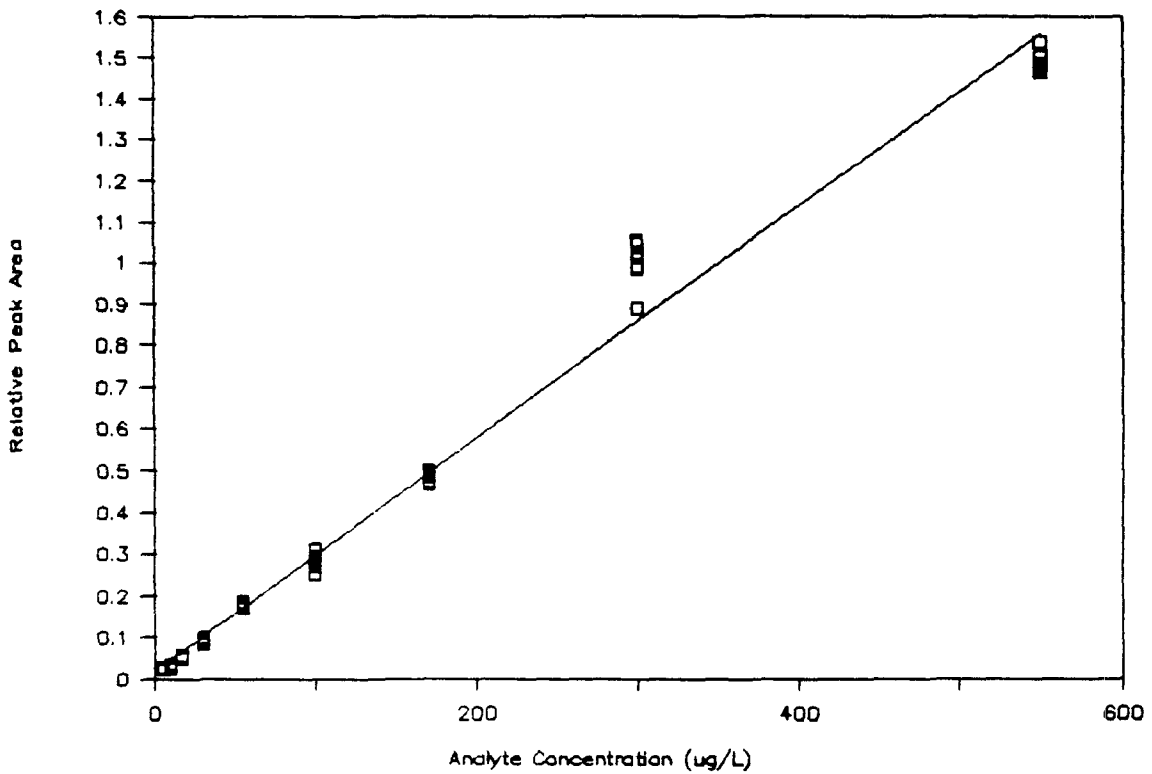
1,3-Dichloropropane
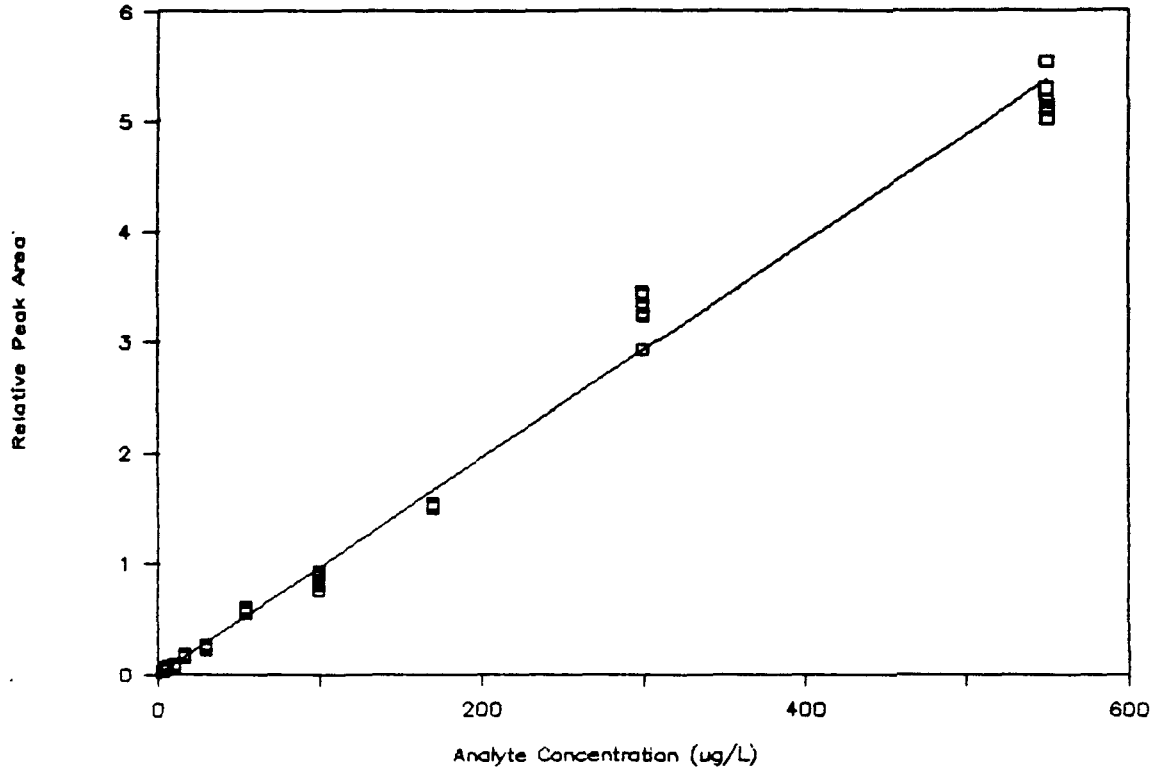
1,1-Dichloropropene
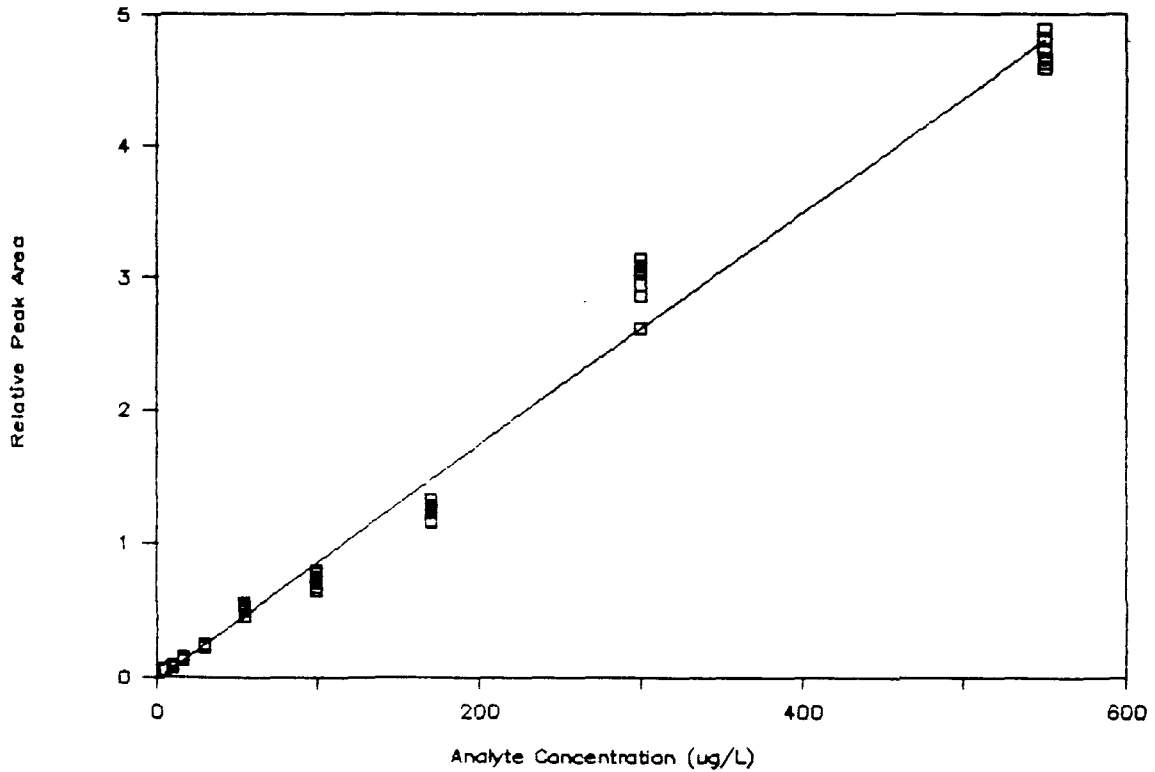
cis−1,3−Dichloropropene

Relative Peak Area vs. Analyte Concentration (ug/L)

trans−1,3−Dichloropropene

Relative Peak Area vs. Analyte Concentration (ug/L)

A-22

1,2-Dimethylbenzene

Relative Peak Area vs. Analyte Concentration (ug/L)

1,4-Dimethylbenzene

Relative Peak Area vs. Analyte Concentration (ug/L)
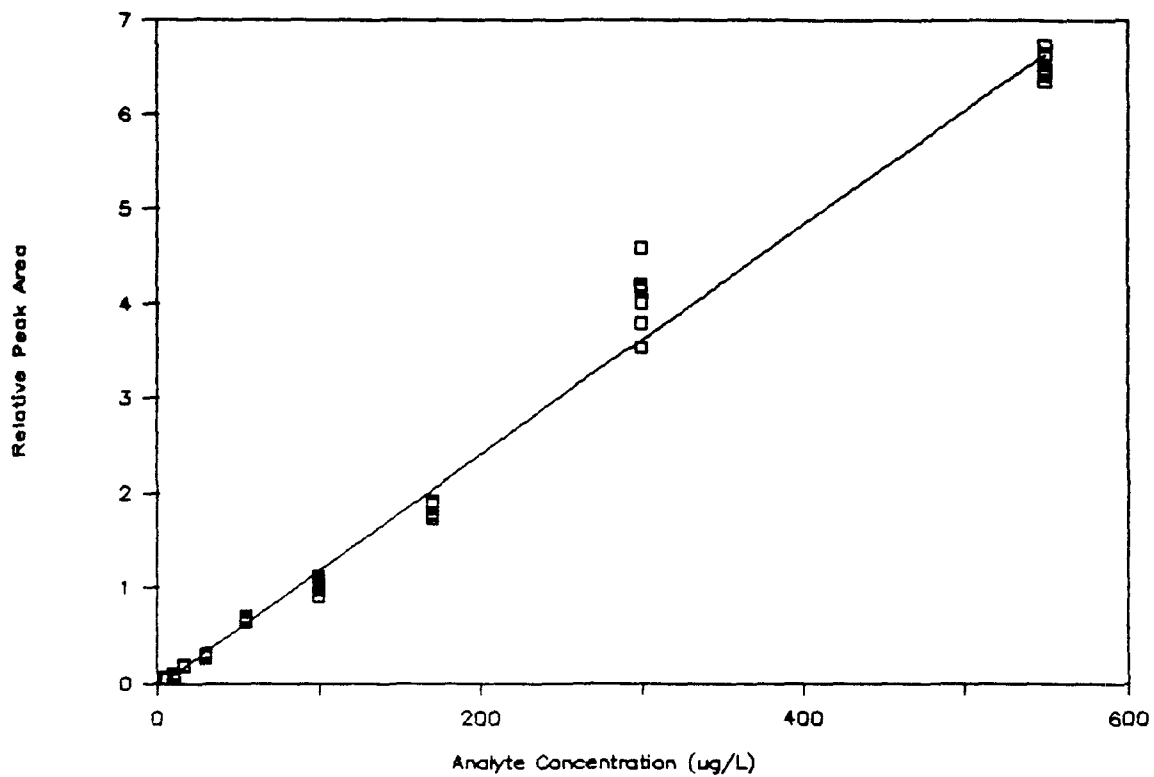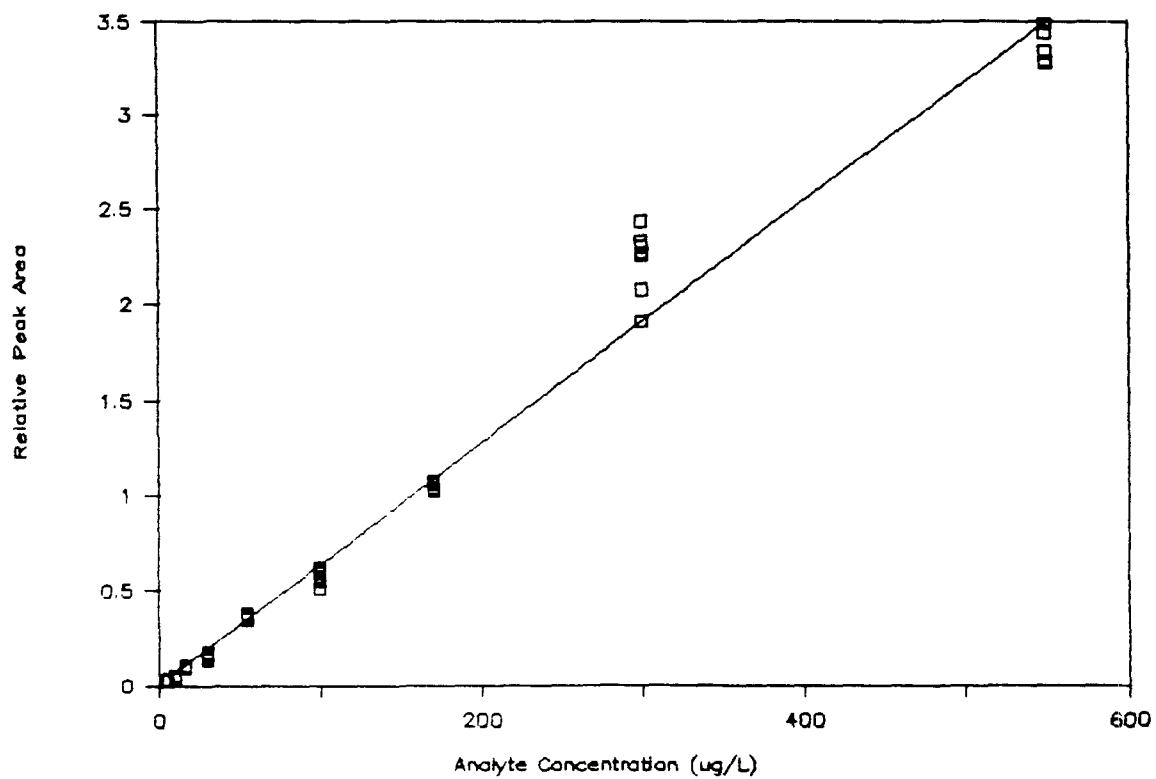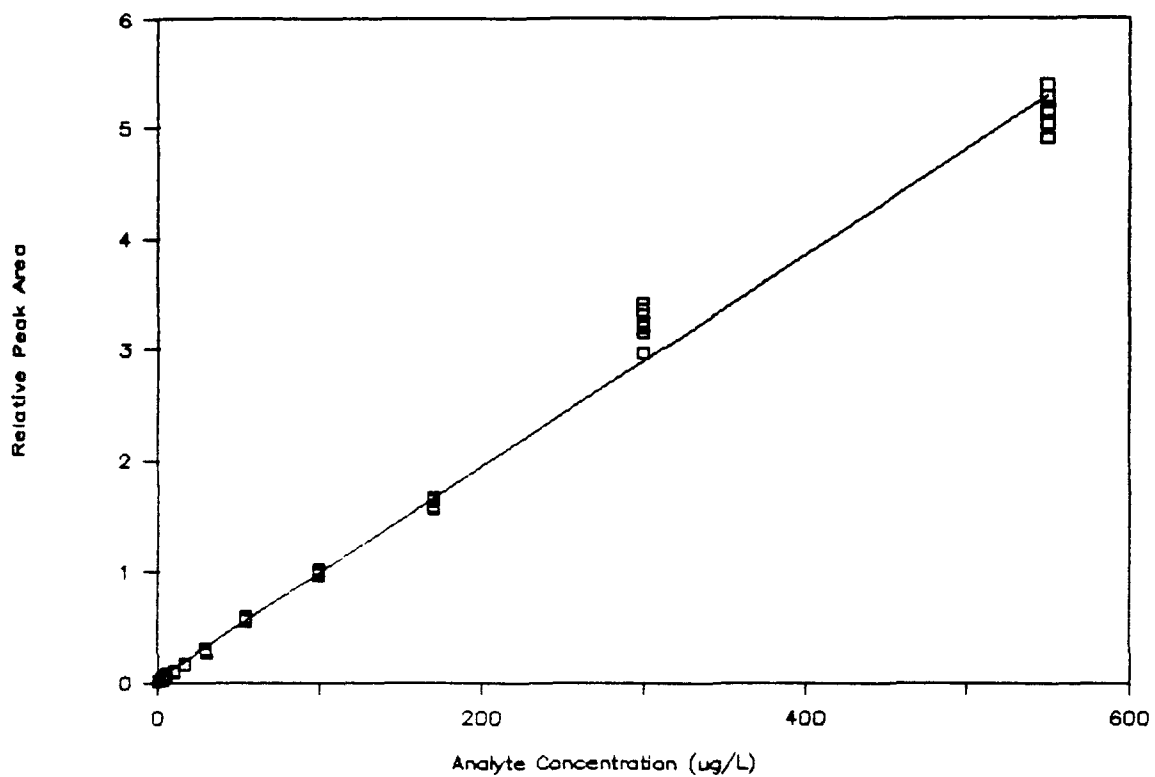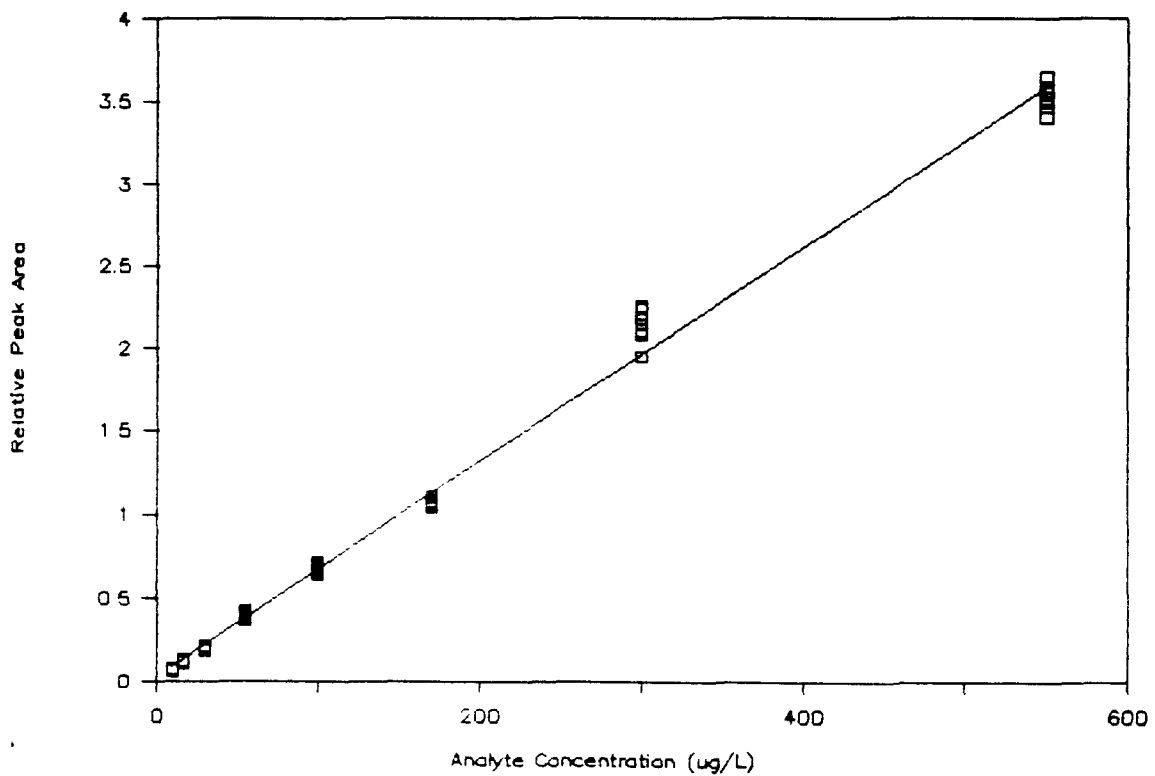
Ethyl methacrylate

Ethylbenzene

A-24
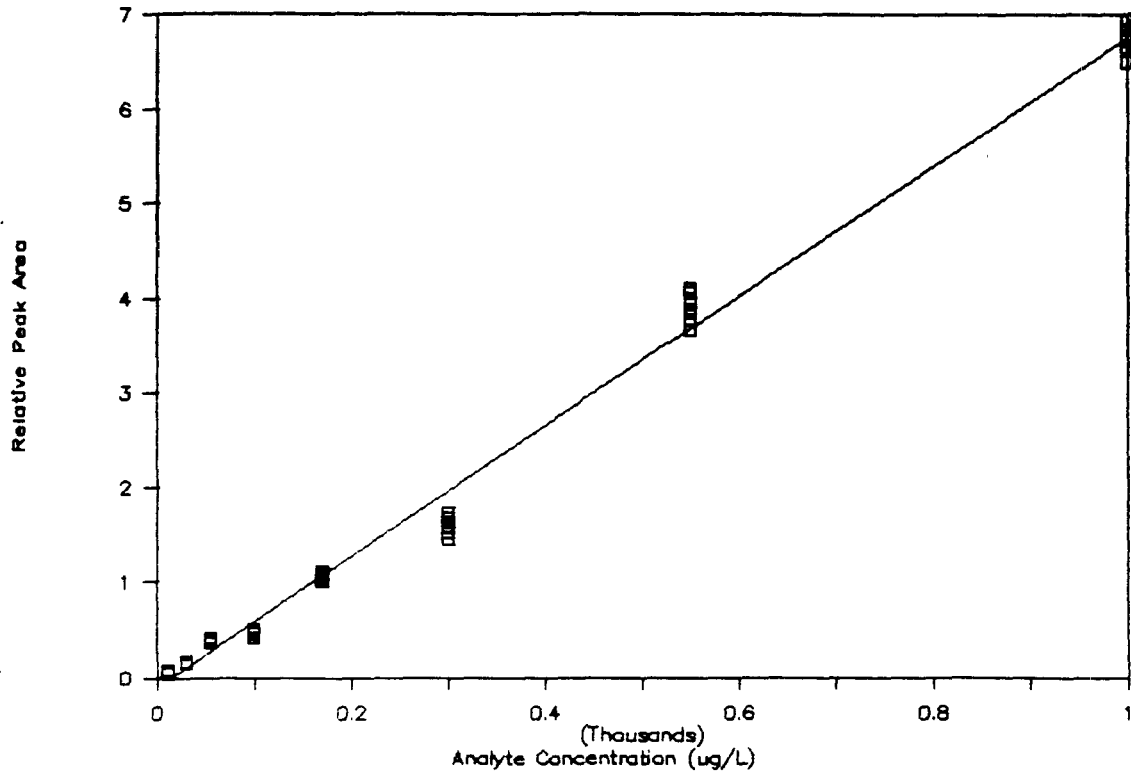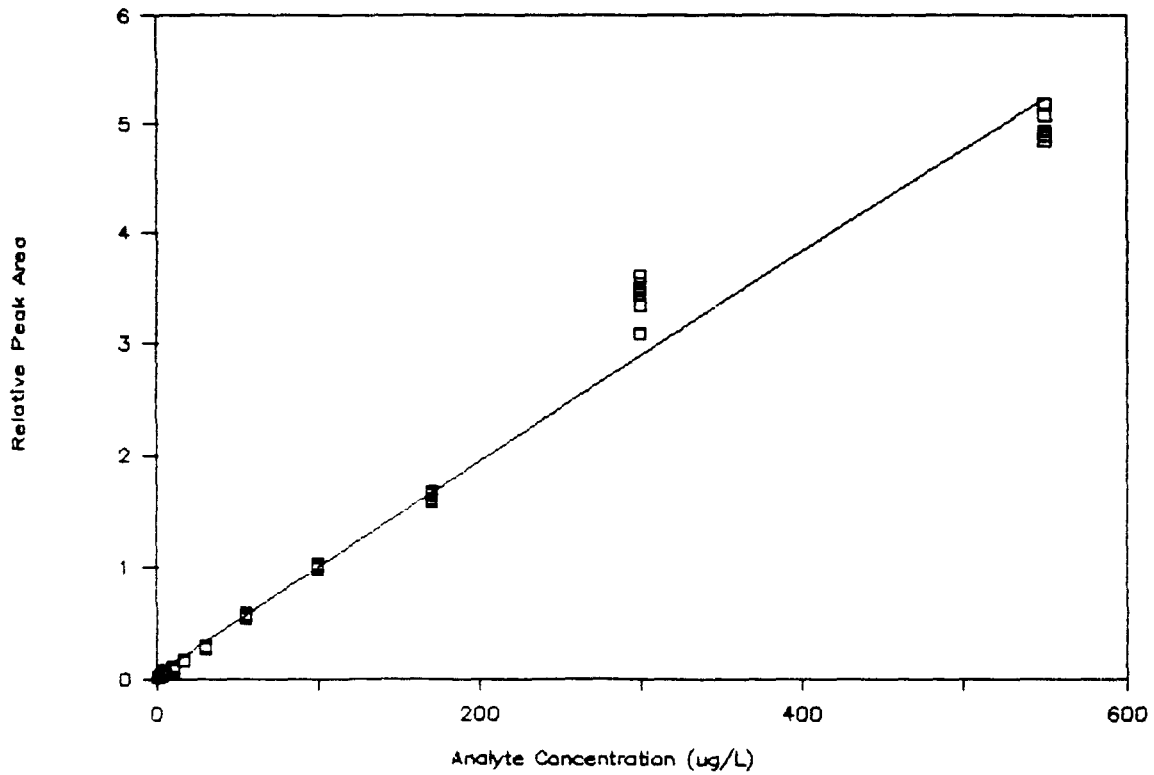
Hexachlorobutadiene
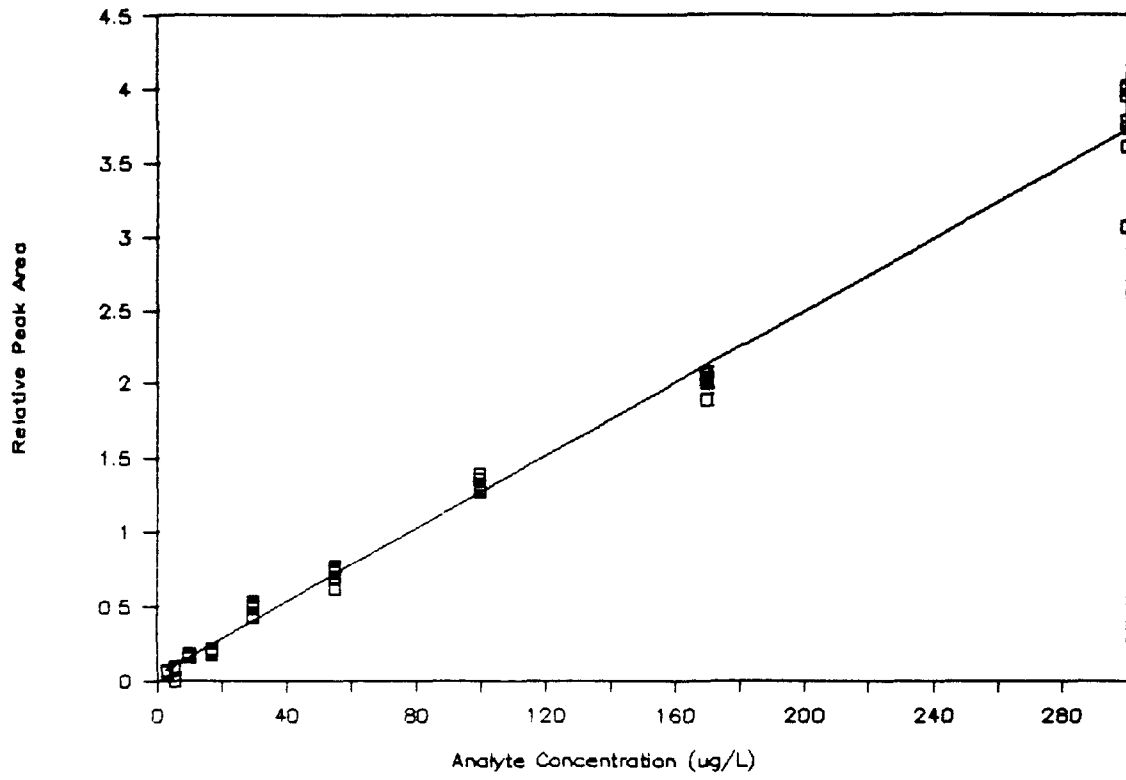
Hexachloroethane
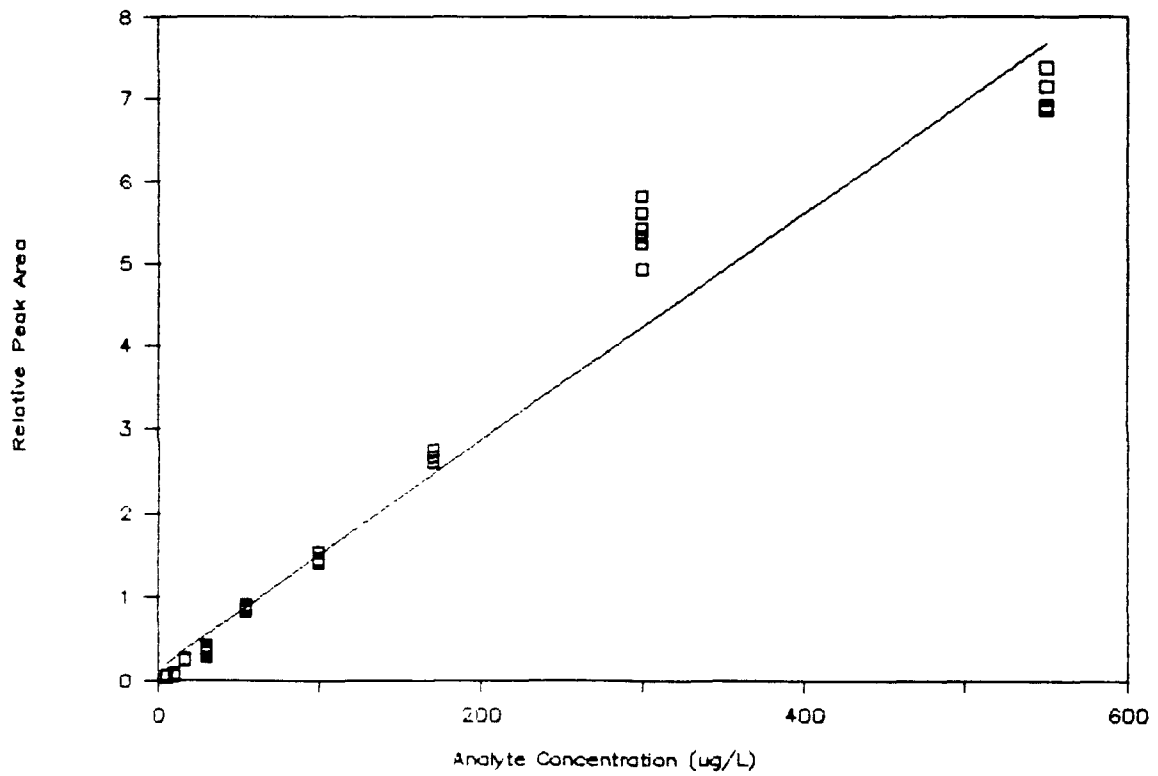
Hexachloropropene
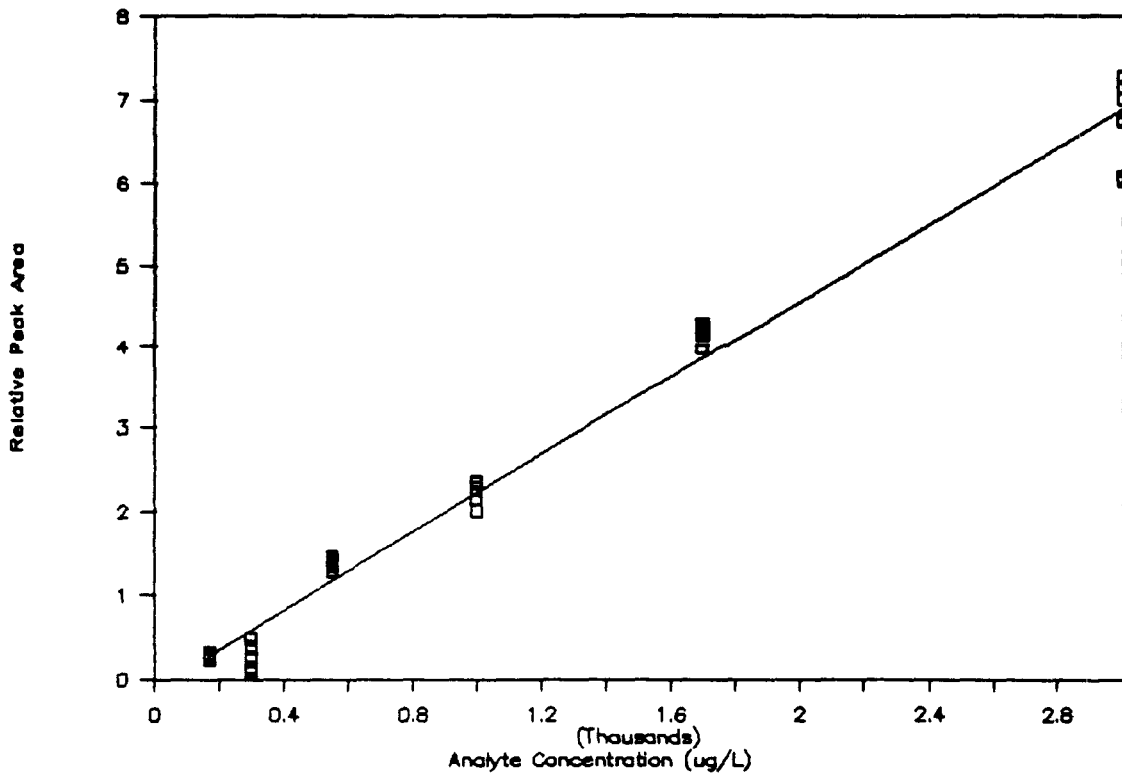
2-Hexanone
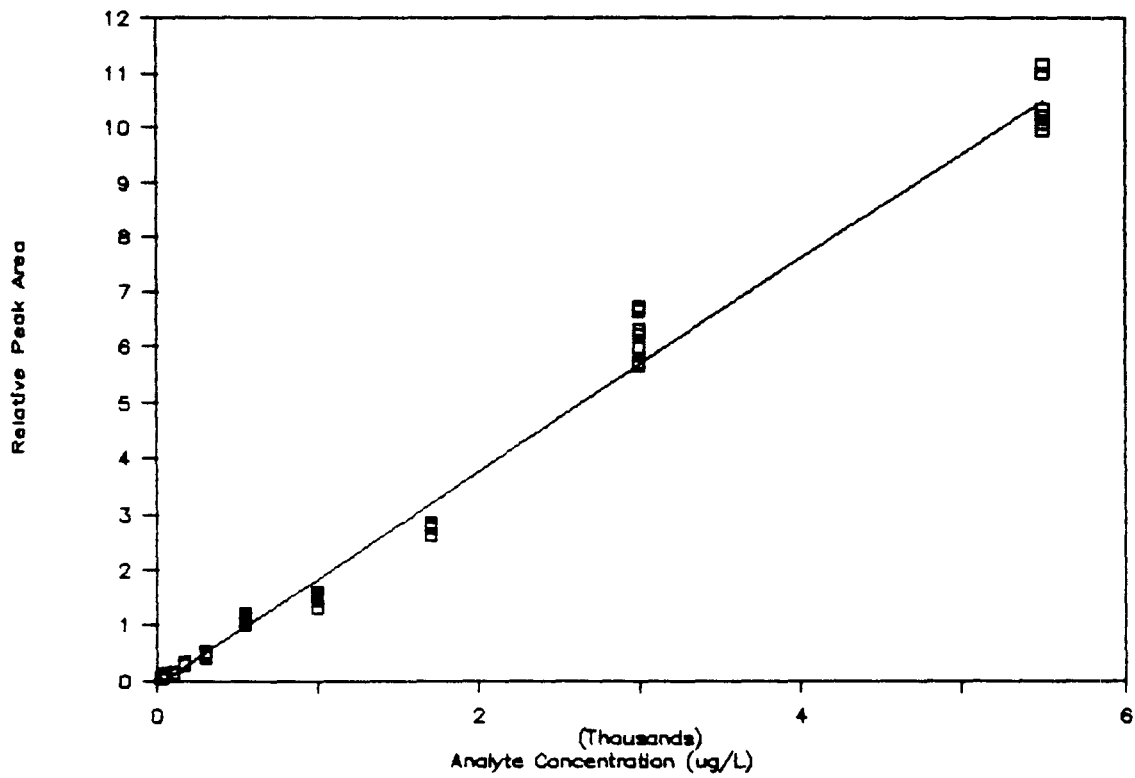
Iodomethane
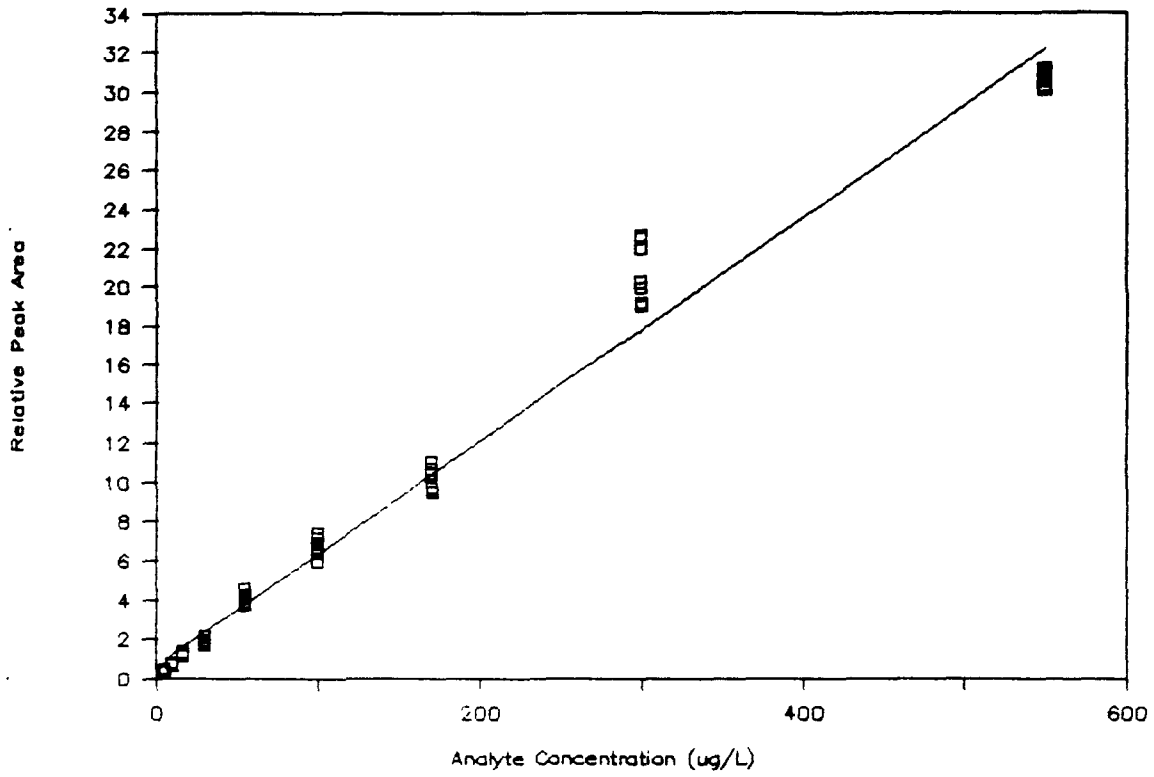
Isopropylbenzene
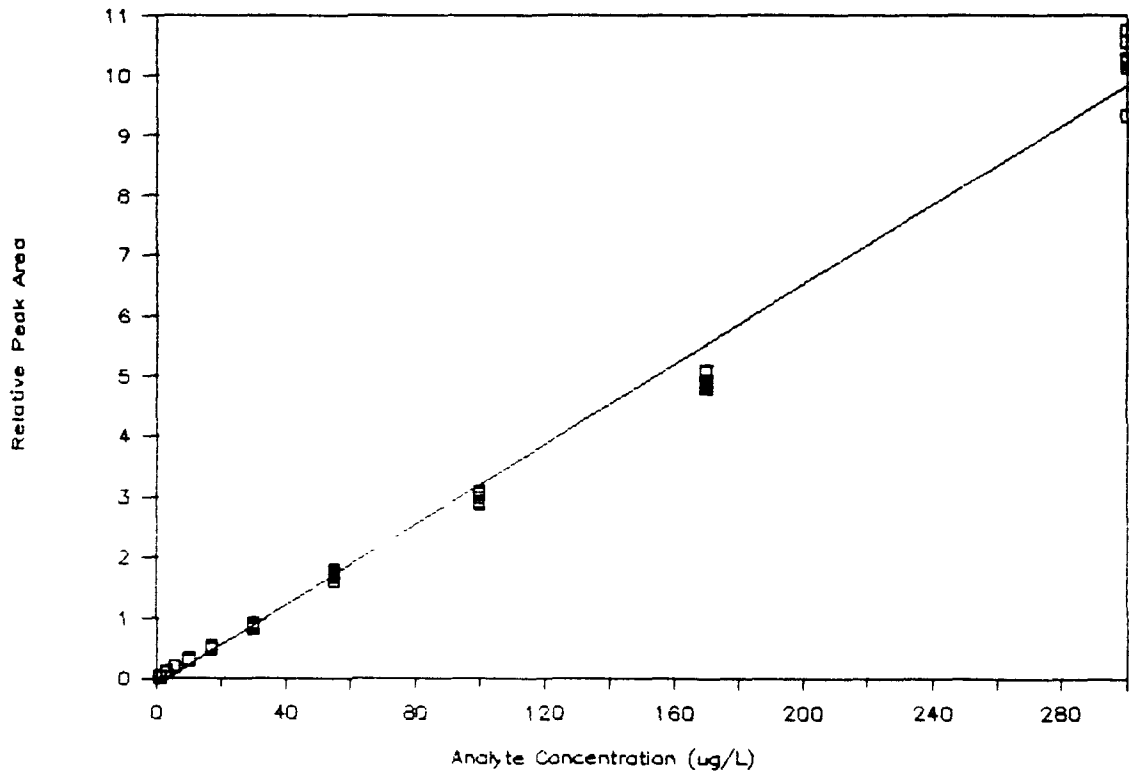
p—Isopropyltoluene

Methacrylonitrile

A-28
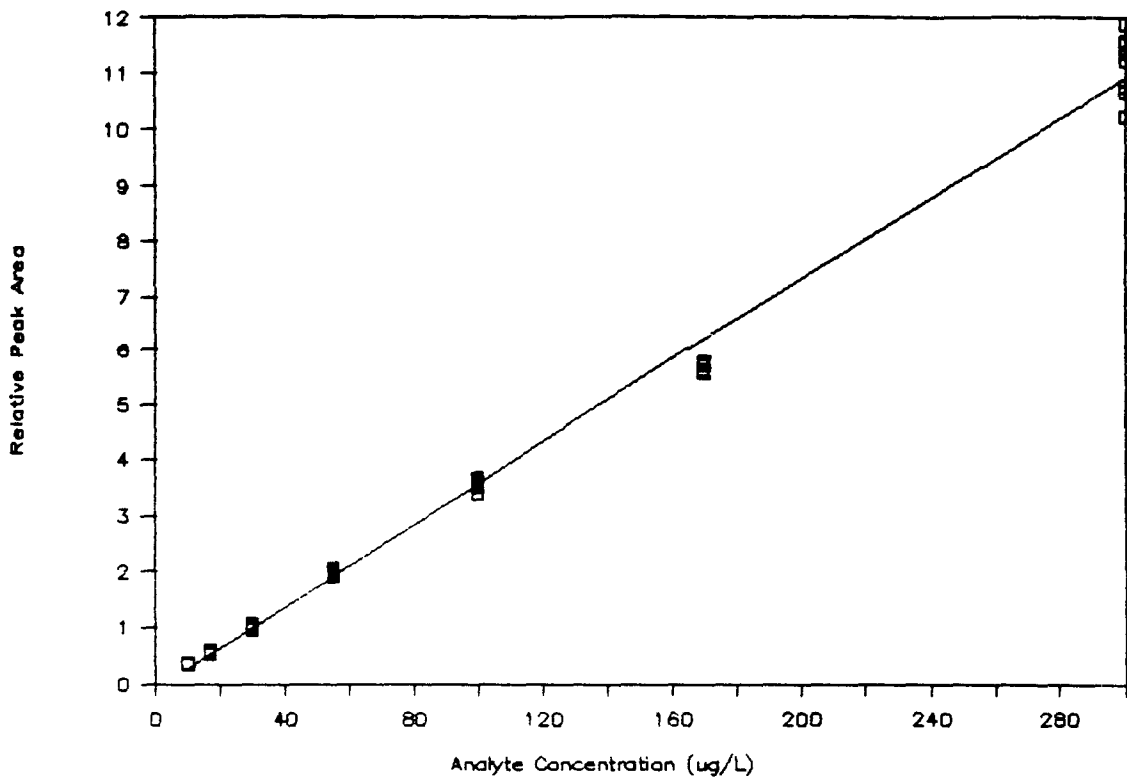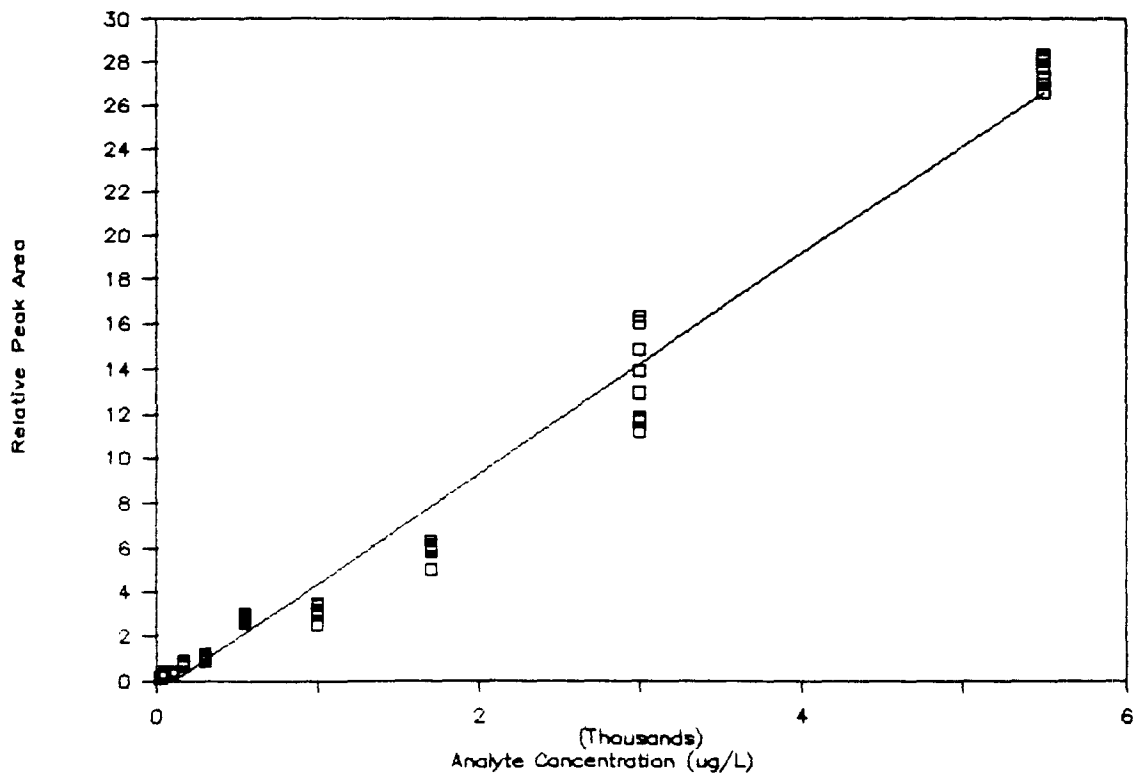
Methyl methacrylate
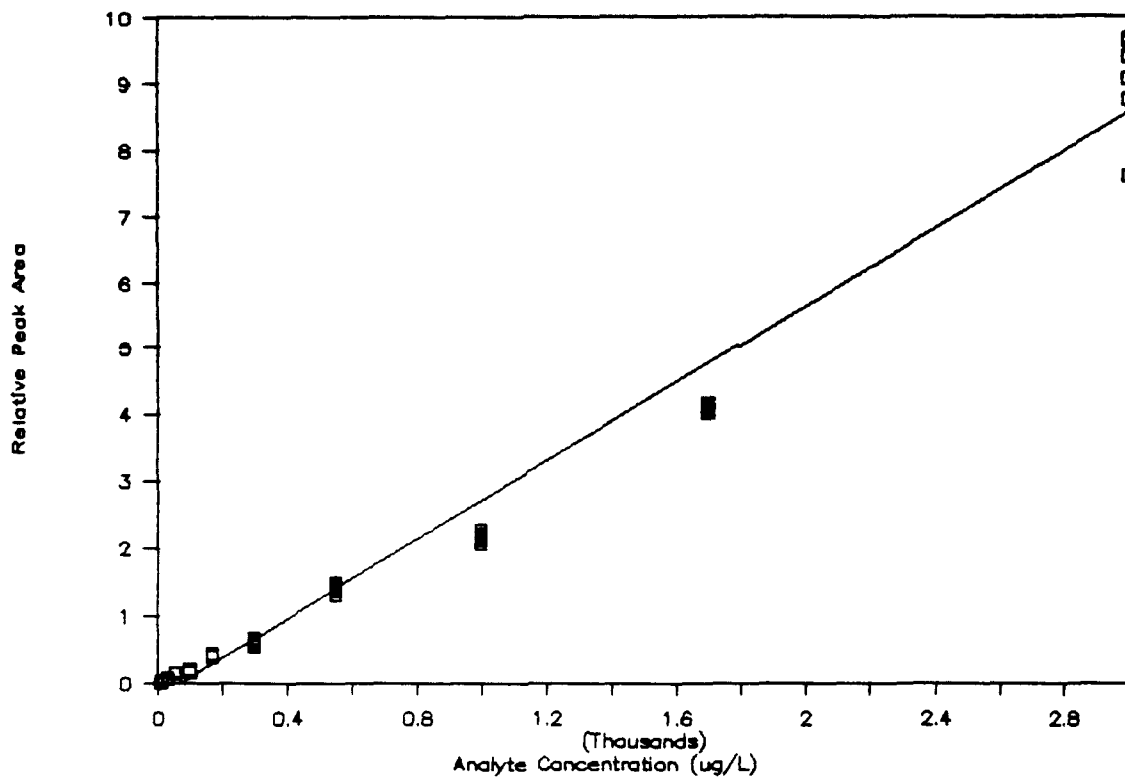
4-Methyl-2-pentanone
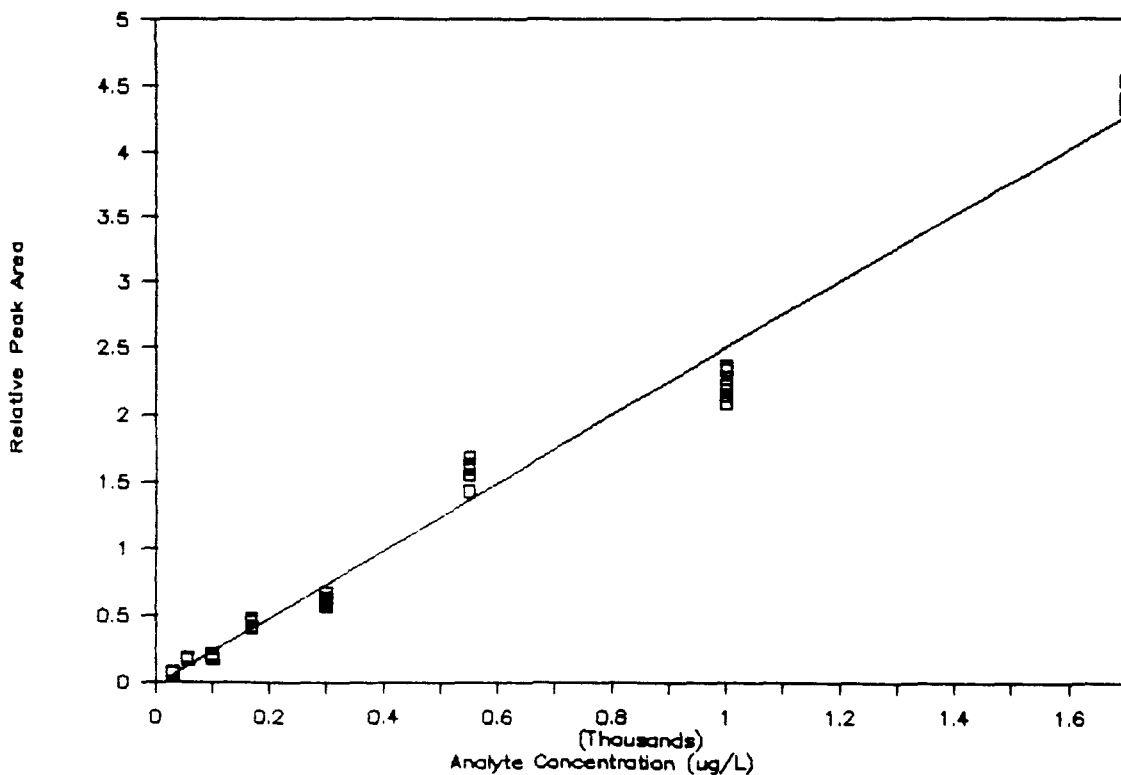
Naphthalene
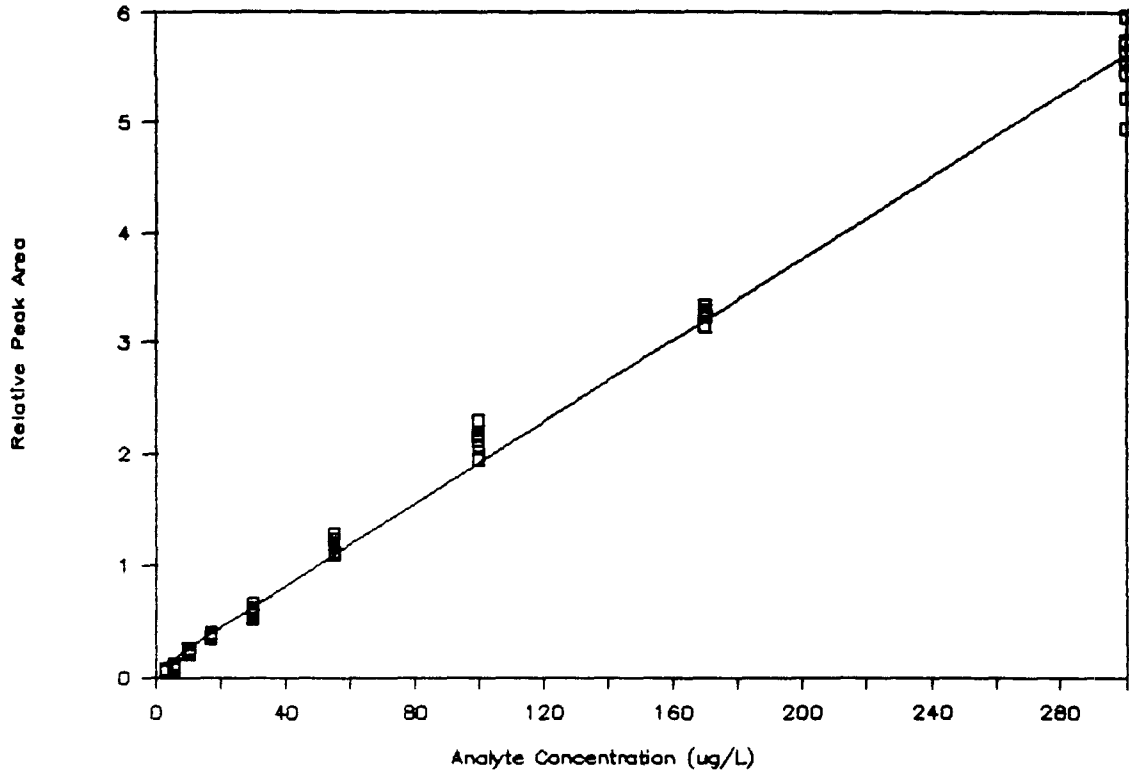
Propionitrile
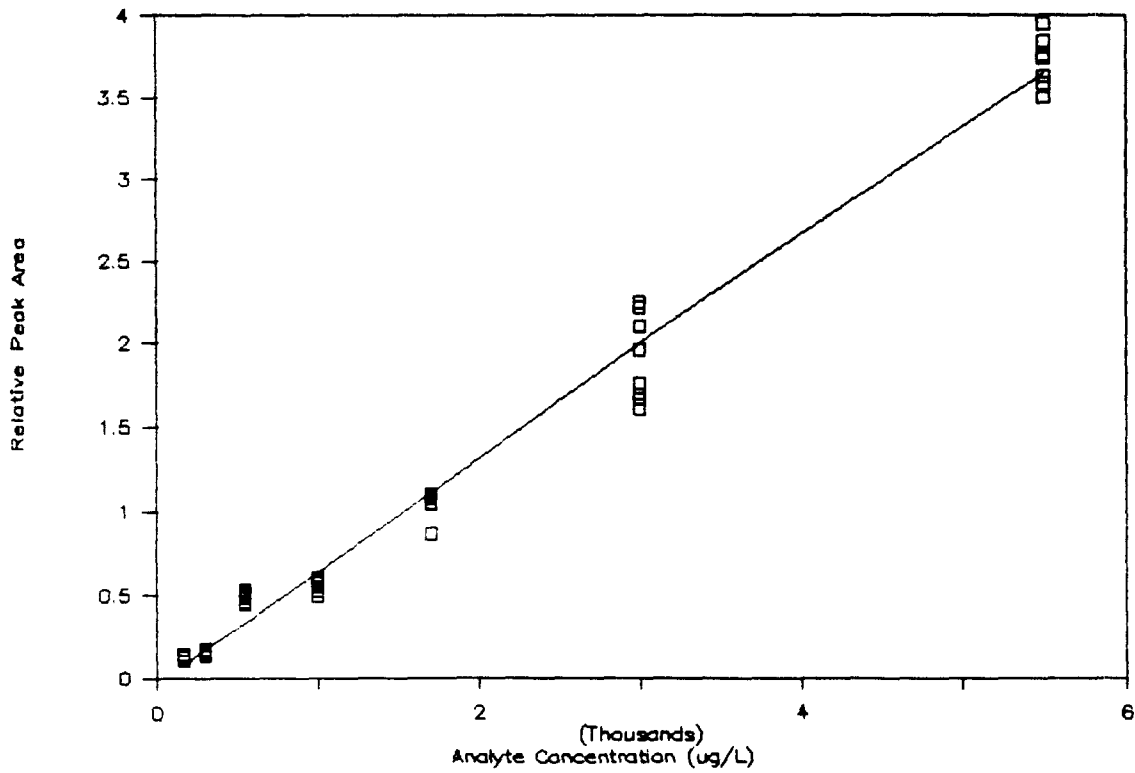
n-Propylbenzene
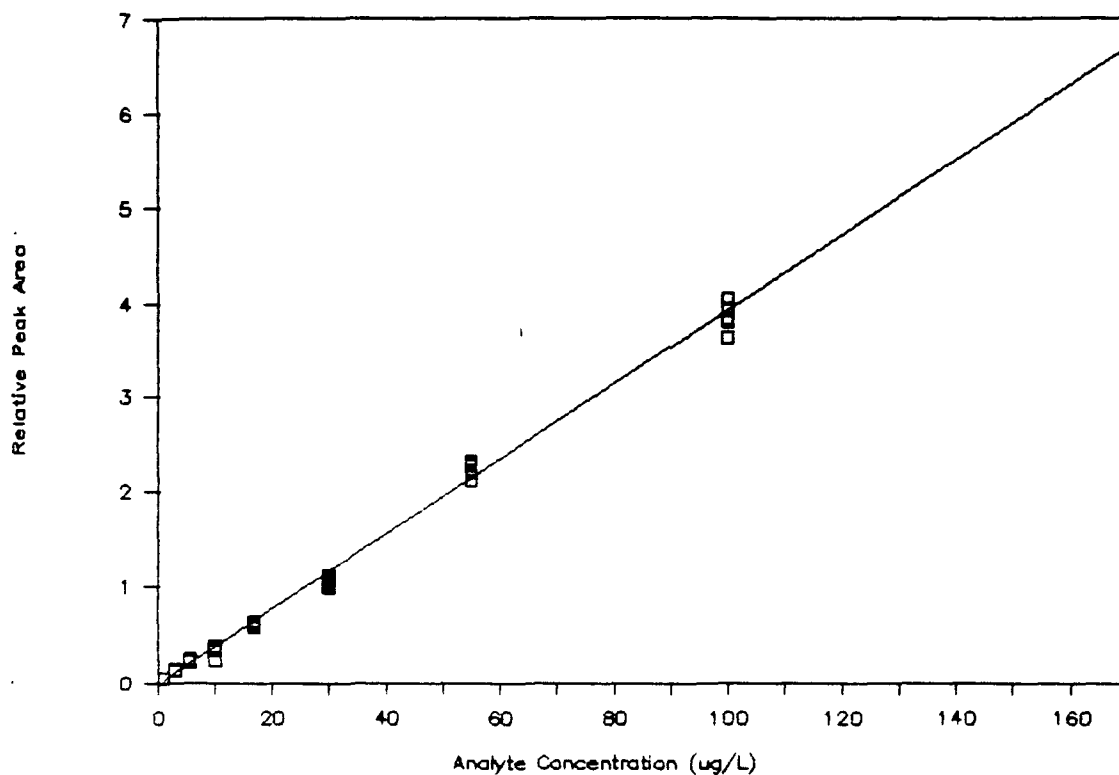
Styrene
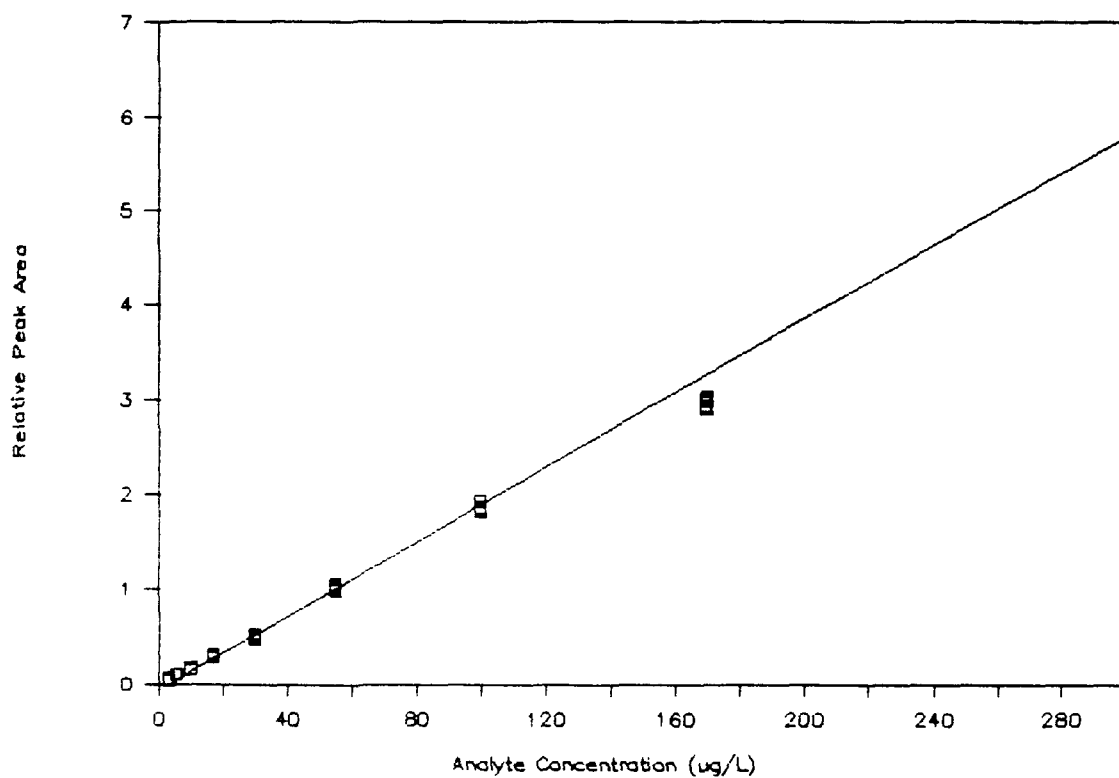
1,1,1,2-Tetrachloroethane
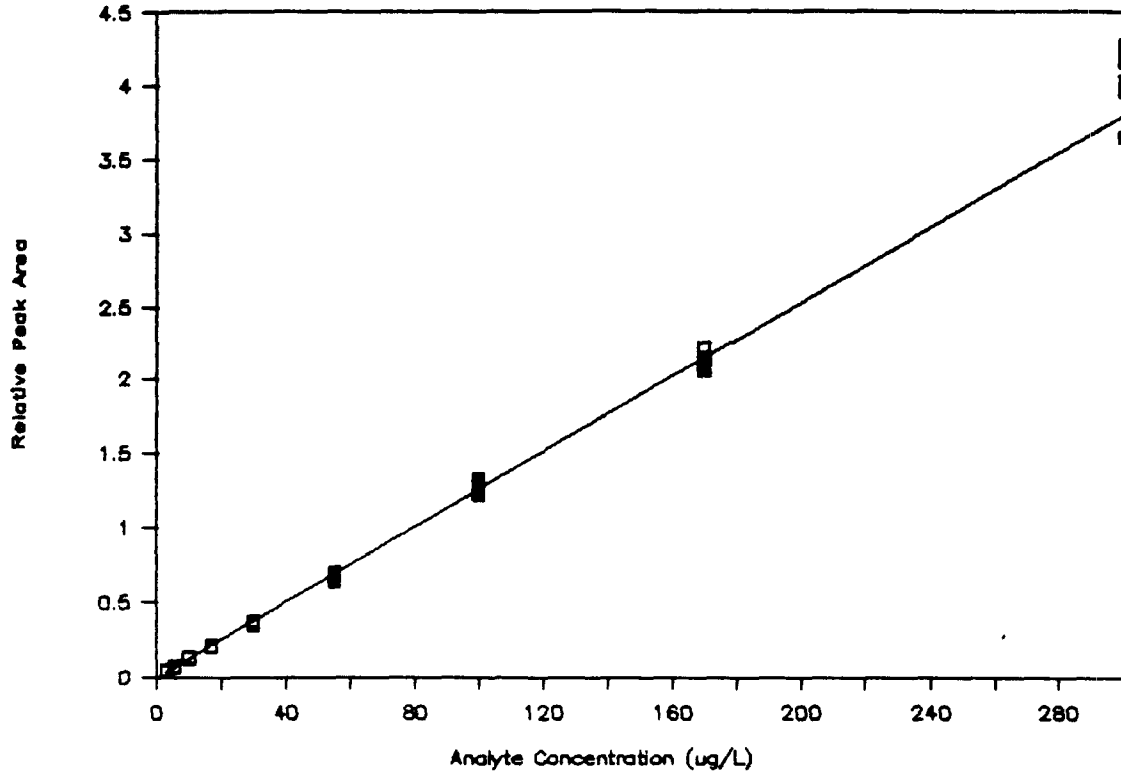
1,1,2,2-Tetrachloroethane
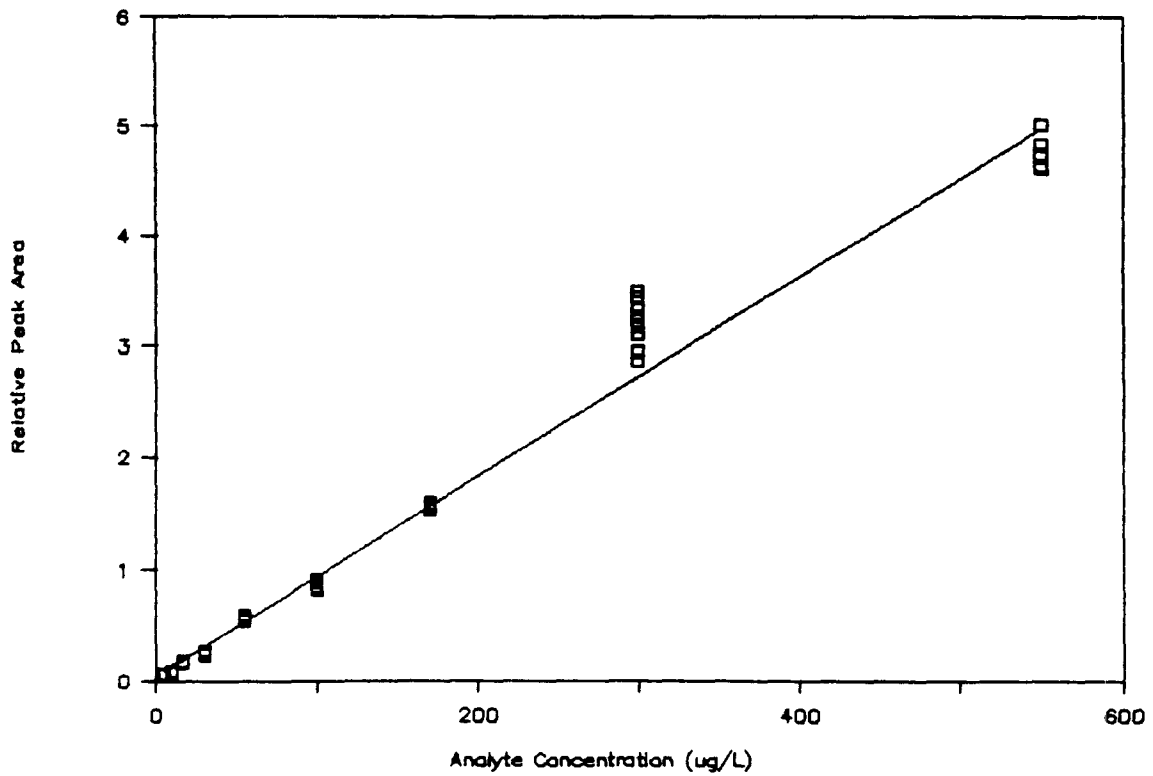
Tetrachloroethene
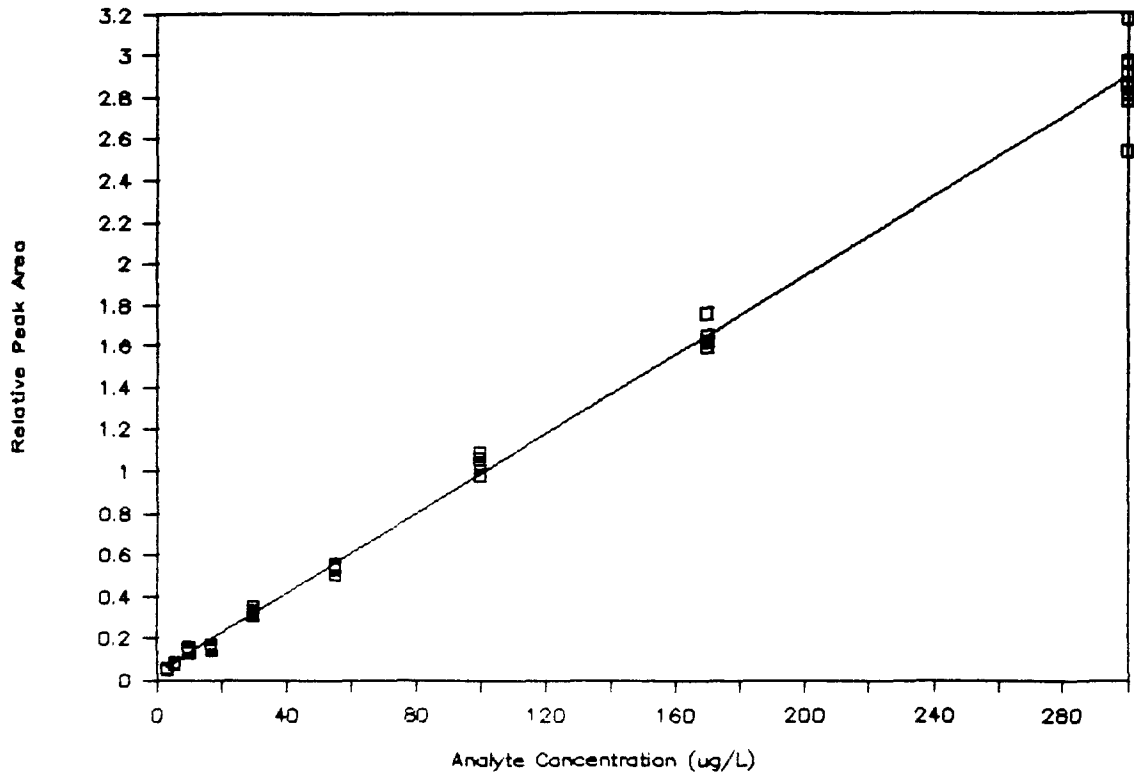
Toluene
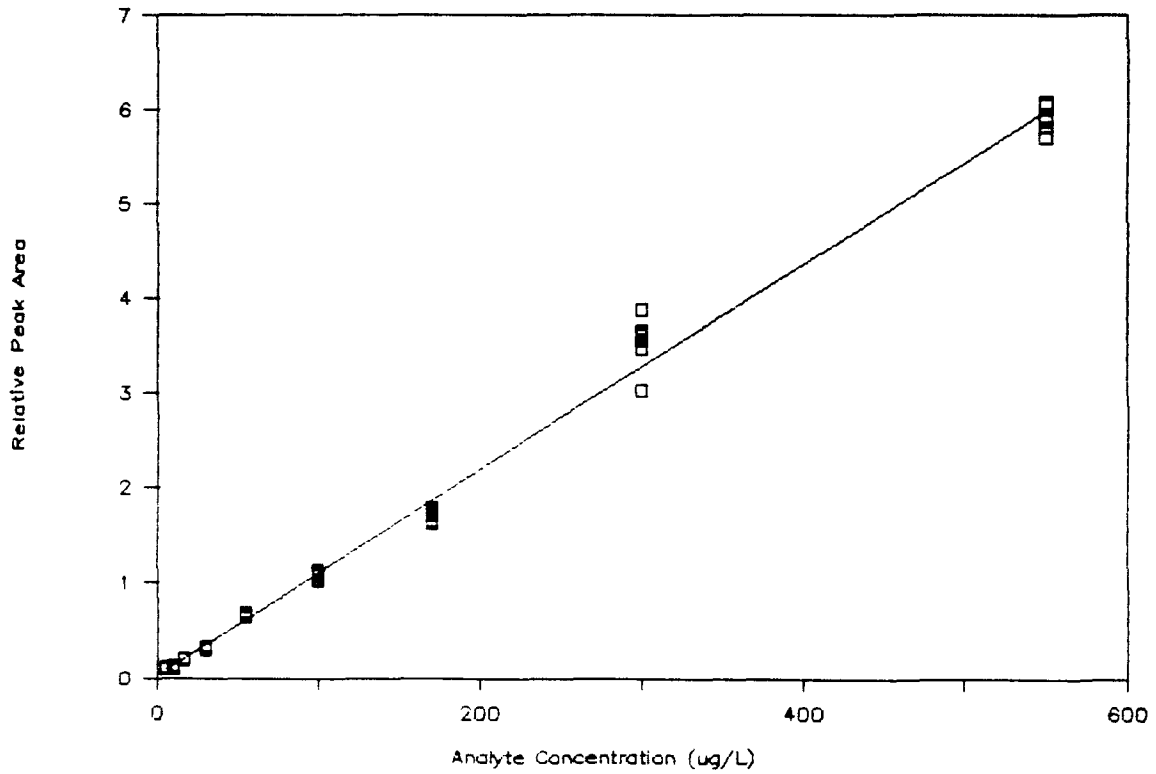
1,2,4-Trichlorobenzene
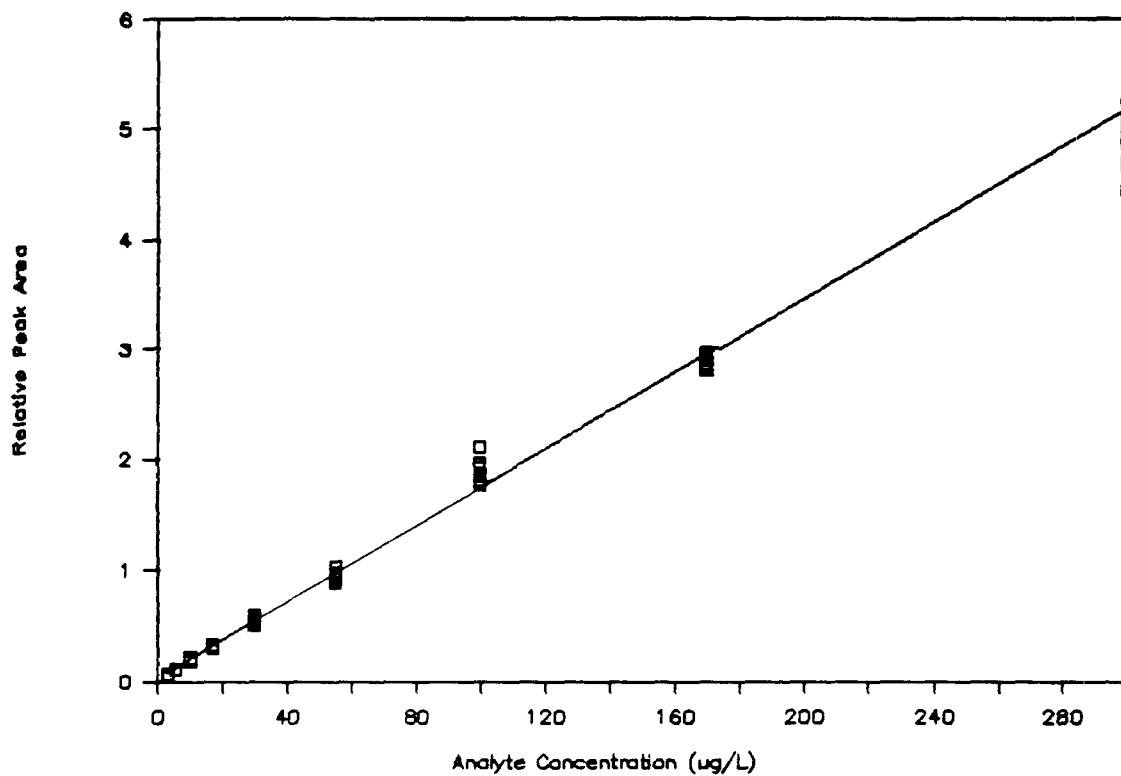
Tribromomethane
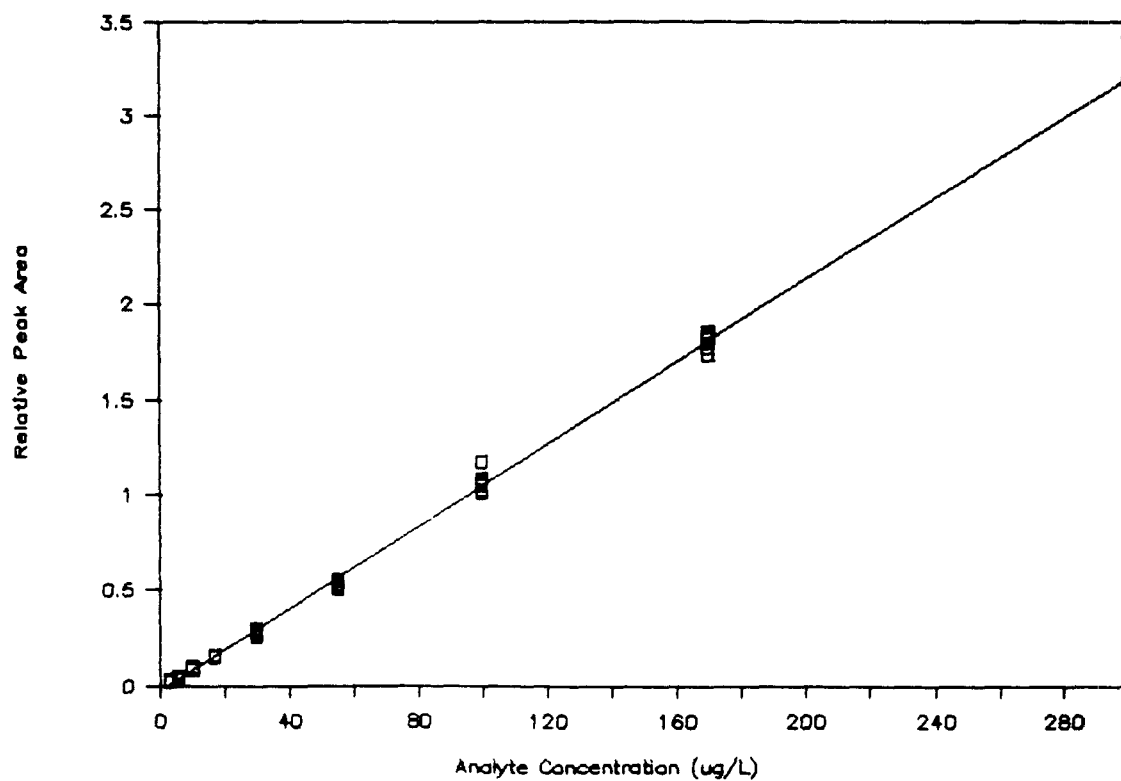
1,1,1-Trichloroethane
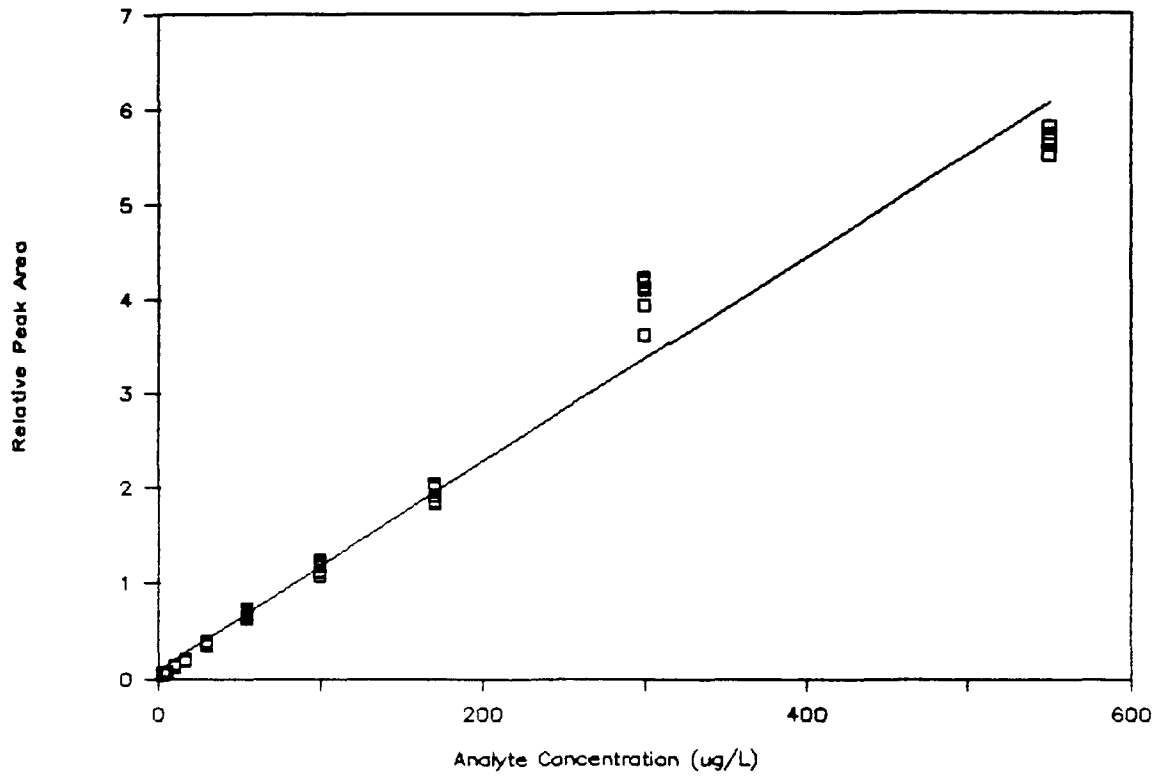
1,1,2-Trichloroethane
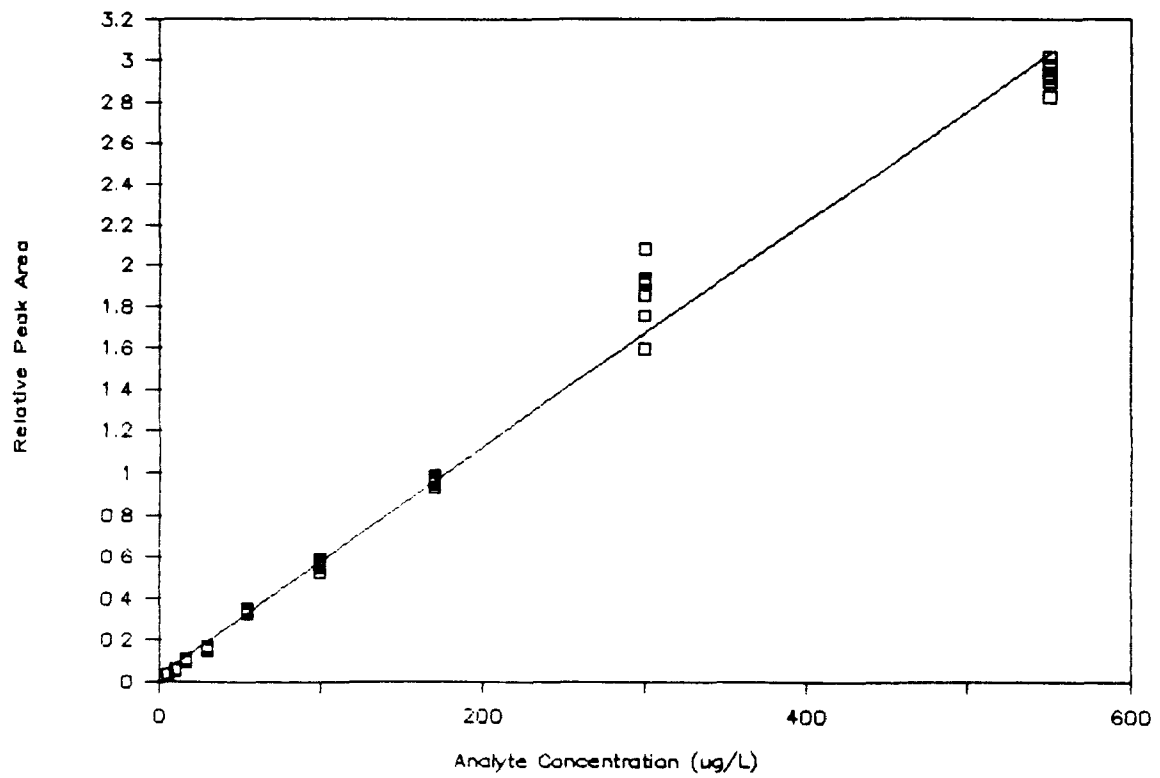
Trichlorofluoromethane

Trichloroethene

A-36
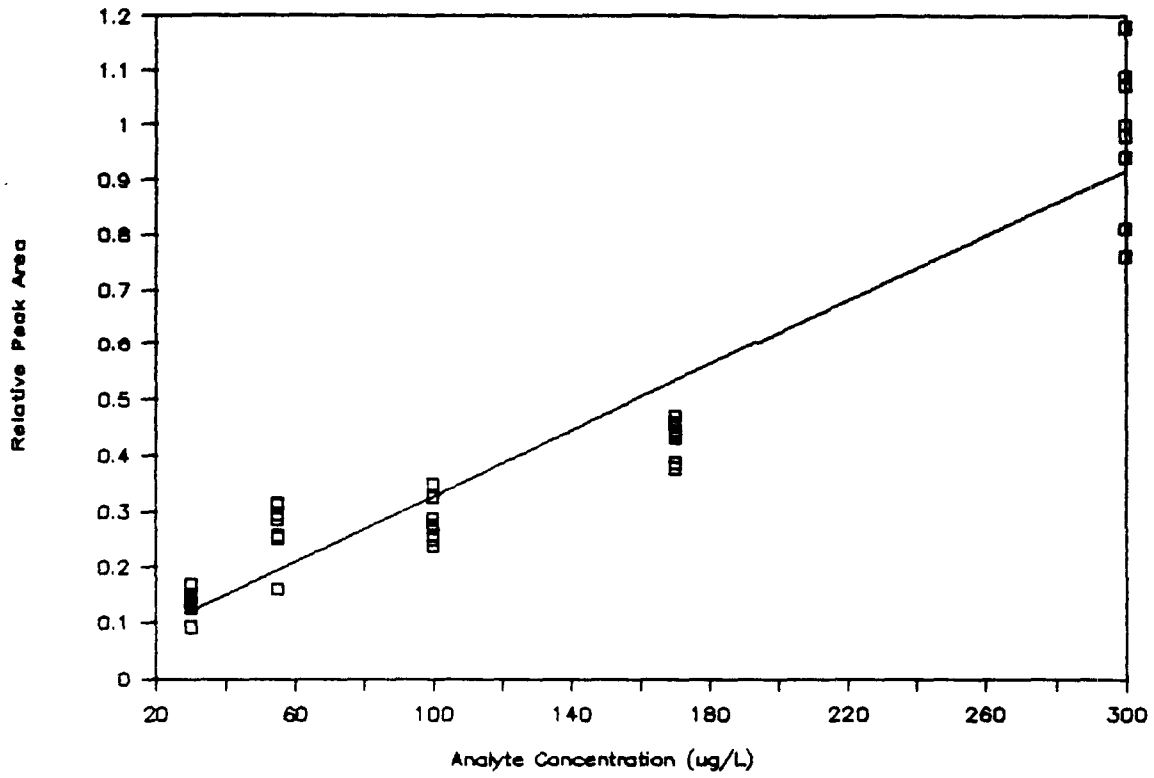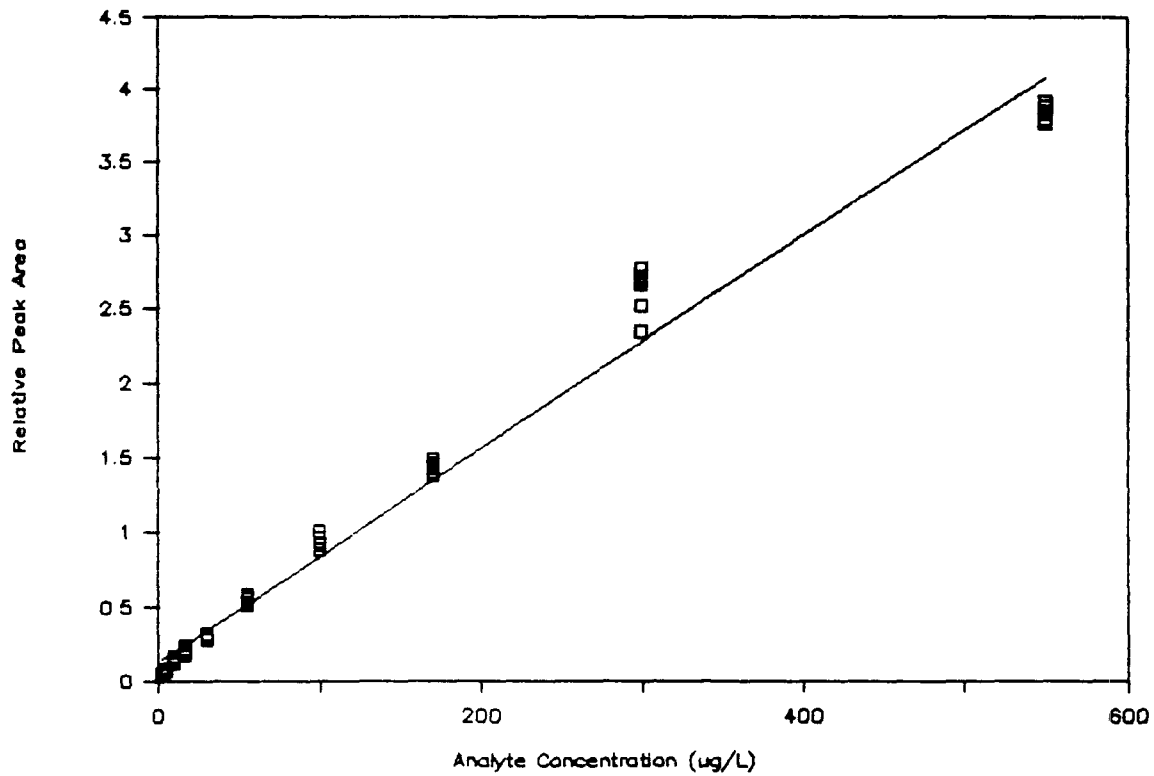
1,2,3-Trichloropropane
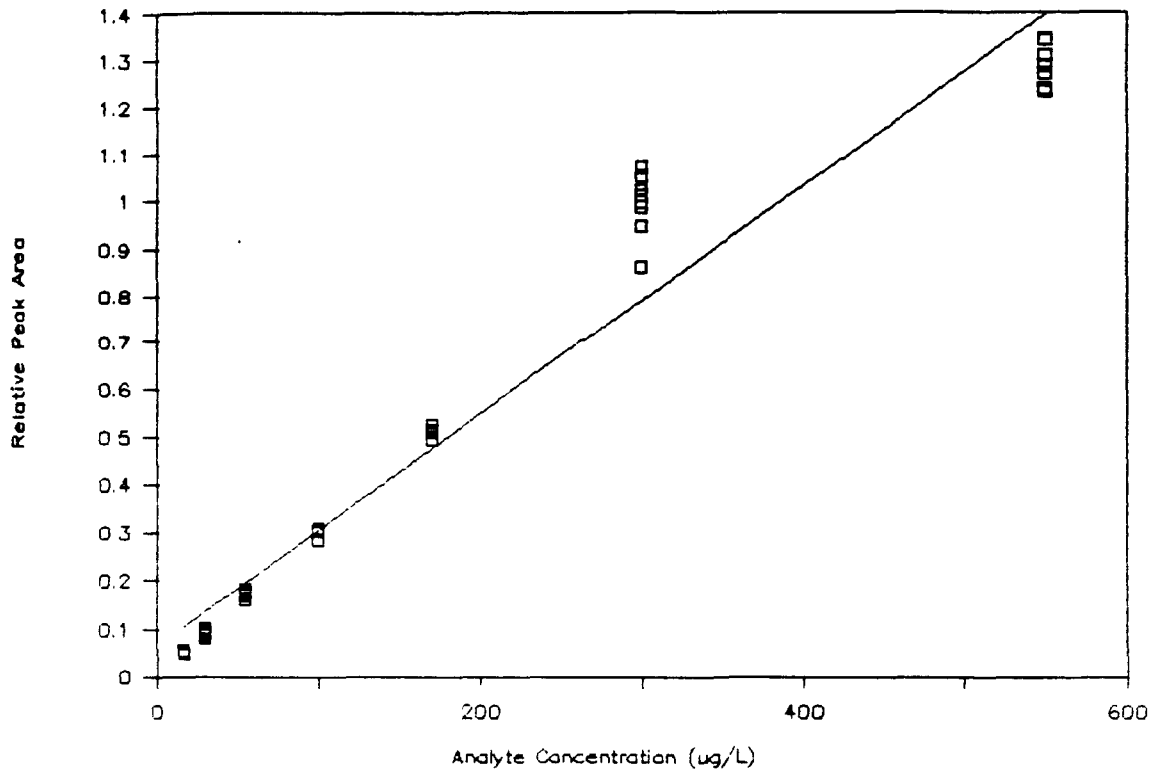
1,2,4-Trimethylbenzene

1,3,5—Trimethylbenzene

Relative Peak Area vs Analyte Concentration (ug/L)

Vinyl acetate

Relative Peak Area vs (Thousands) Analyte Concentration (ug/L)

Vinyl chloride

PB88245881

BA

BIN: M316   03-23-98
INVOICE: 569144
SHIPTO: 1*89259
PAYMENT: NONE