

United States  
Environmental Protection  
Agency

Office of Water  
(WH-552)

EPA-821-R-93-015  
September 1993



# Oil and Grease Workshop

Boston, Massachusetts

June 30, 1993



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## **DISCLAIMER**

This report has been reviewed by the Analytical Methods Staff of the EPA Office of Water. It is intended to inform the public about EPA's efforts to replace Freon-113 in Agency analytical methods. Mention of company names, trade names or commercial products does not constitute endorsement or recommendation for use.

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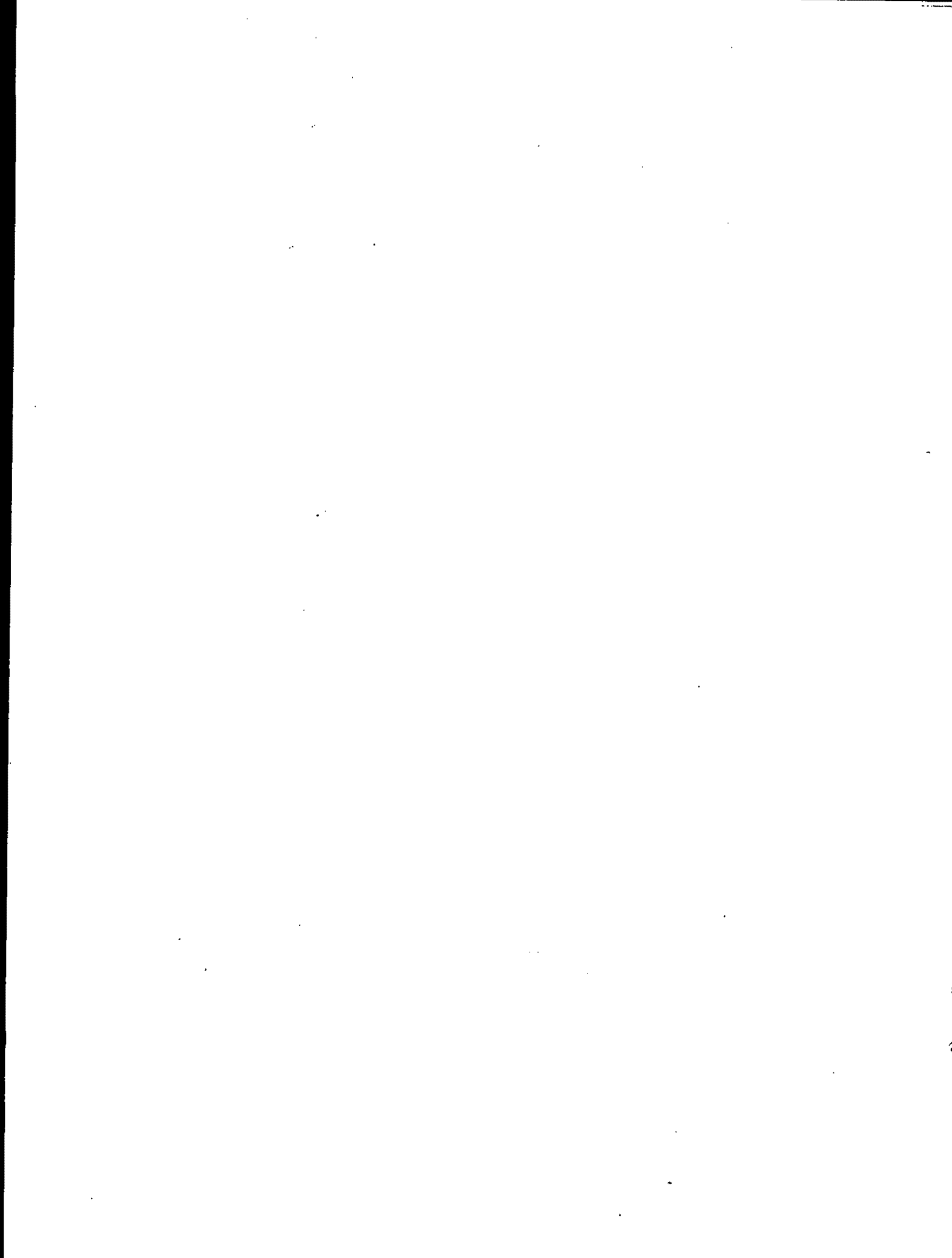
## **ACKNOWLEDGEMENTS**

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**MEETING SUMMARY  
OIL AND GREASE WORKSHOP  
BOSTON, MASSACHUSETTS  
JUNE 30, 1993**

**ANALYTICAL METHODS STAFF  
ENGINEERING AND ANALYSIS DIVISION  
OFFICE OF SCIENCE AND TECHNOLOGY  
OFFICE OF WATER  
U.S. ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460**





## Introduction

The Analytical Methods Staff of the Office of Science and Technology's Engineering and Analysis Division (within the U.S. EPA Office of Water), held a public workshop on the subject of the Agency's Oil and Grease Freon Replacement Study at the EPA Region I Conference Center in Boston, Massachusetts on June 30, 1993.

The Oil and Grease Workshop was intended to inform the public about EPA's efforts to find a replacement for Freon 113 in its analytical methods for oil and grease, and to provide a forum for public comment. The date, time, place and purpose of the workshop were advertised in the *Federal Register* on June 8, 1993.

The Oil and Grease Freon Replacement Study, is more fully described in a report entitled *Preliminary Report of EPA Efforts to Replace Freon for the Determination of Oil and Grease*, EPA-821-R-93-009, June 1993. Briefly, EPA is seeking a replacement solvent for Freon 113 in three Agency methods for "total recoverable oil and grease" because production and sale of Freon 113 and other Class I ozone depleting substances will be banned by January 1, 1996 under both the Clean Air Act Amendments of 1990 and the Montreal Protocol on Substances that Deplete the Ozone Layer. The Freon Replacement Study is a cooperative effort among the EPA Offices of Water, Solid Waste, and Air and Radiation, with the voluntary participation of a number of instrument manufacturers and vendors. The first phase of the study involved exploration of the use of five alternative solvents and two alternative techniques that were tested on a suite of actual industrial and commercial aqueous and solid waste samples. The results of EPA's statistical analysis of the Phase I study data for conventional and alternative techniques were presented at the workshop.

## Meeting Summary

This document summarizes the information presented at the workshop by EPA and invited speakers, as well as questions and comments from the audience. The workshop agenda is attached as Appendix A. The visual aids used by the speakers are provided in Appendices B through H.

**Welcome:** *Kevin McSweeney, U.S. EPA Region I*

Mr. McSweeney welcomed the participants to Boston and introduced Mr. Telliard as the workshop chairman.

**Freon Replacement Method Study:** *William A. Telliard, U.S. EPA Office of Science and Technology*

The first speaker was William A. Telliard, Chief of the Analytical Methods Staff within the Office of Water's Engineering and Analysis Division. Mr. Telliard is responsible for direction of the Oil and Grease Freon Replacement Study.

Mr. Telliard reviewed the regulatory history of chlorofluorocarbons, including the 1990 Clean Air Act Amendments (CAAA) and the Montreal Protocol on Substances that Deplete the Ozone Layer. He noted that Freon 113, the solvent used in the oil and grease measurement, is regulated by the CAAA and the Montreal Protocol and will be phased out of use by 1996. He stated that oil and grease is an old method which was first used in sanitary chemistry to study the effects of an Imhoff tank on removing large particulates from sewage to prevent sewer plugging. Mr. Telliard pointed out that oil and grease is a "method-defined" parameter whose result depends on the solvent that is used. Historically, carbon tetrachloride was used, then *n*-hexane, and most recently Freon 113.

He then described Phase I of the Freon Replacement Study. The purpose of the first phase of this study was to continue the Agency's investigation of replacement solvents to identify a solvent that yields results equivalent to Freon 113, or failing that, to select a solvent(s) or alternative technique(s) for further study. The five alternative solvents evaluated in Phase I were *n*-hexane, an 80:20 mixture of *n*-hexane/methyl tertiary-butyl ether, methylene chloride, perchloroethylene, and DuPont 123 (2,2-dichloro-1,1,1-trifluoroethane.)

Mr. Telliard indicated the scope of the problem that EPA faces in changing the oil and grease method by pointing out that oil and grease is a regulated parameter in approximately 10,500 National Pollutant Discharge Elimination System (NPDES) permits and in effluent guidelines for 25 industries. He stated that in order to obtain realistic results, Phase I of the study tested "real world" samples from 39 plants in 24 industrial categories, including approximately 41 aqueous wastes and 30 solid wastes. These samples represented oil and grease

of animal, vegetable and mineral (petroleum) origin. He noted that both solid phase extraction (SPE) and infrared techniques were evaluated in the first phase of the study. He stated that all of the industrial plants that had been visited and sampled were effectively removing oil and grease from their effluents with the treatment equipment they had installed. Many plants had to be sampled upstream from the final effluent to detect significant amounts of oil and grease. *Mr. Telliard's presentation materials may be found in Appendix B.*

Mr. Telliard then introduced Roger Litow, who was to speak on the statistical analysis of the Phase I study data.

#### **Statistical Analysis of Phase I Study Data: *Roger Litow, DynCorp Viar, Inc.***

Mr. Litow discussed the results of the statistical analysis of the study data. He began by discussing the statistical measures of similarity between solvents that were used in the study and described in the June 1993 report distributed to the workshop participants. He explained that the "solvent- to-Freon ratio" used in the report is not the primary measure of similarity because it does not account for variability in the data and tends to cancel out the effects of samples whose alternative solvent results were higher than Freon for some samples and lower for others. Mr. Litow explained that the solvent-to-Freon ratio was used in an attempt to find "correction factors" to convert alternative solvent results to be equivalent to Freon.

He then described the data transformation that was needed to make the study data amenable to analysis of variance (ANOVA). He noted that the variability of the results increases with increasing concentration, rather than being constant (this violates the assumptions of ANOVA). To compensate for this problem, he stated that the data had been log-transformed to eliminate this "heteroscedasticity". A constant was added to bring negative results above zero so that logarithms could be taken. The constant also reduced the influence of the lower results on the ANOVA.

Mr. Litow then described the Root Mean Square Deviation (RMSD), which was used as the primary measure of statistical similarity between Freon 113 results and alternative solvent or technique results. He noted that this measure accounts for variance both above and below the results obtained with Freon 113.

He then recounted the stratification of the study data to find groupings for which equivalent results for Freon 113 and other methods could be expected. Petroleum and non-petroleum were the strata chosen. He presented three graphs (Exhibits 11-13 of the June 1993 report) showing RMSD results versus Acceptance Limits for aqueous samples by separatory funnel extraction and for solid samples by Soxhlet and sonication extractions. He noted that *n*-hexane and perchloroethylene were equivalent to Freon 113 in aqueous samples contaminated with non-petroleum-based oil and grease. For Soxhlet extractions, *n*-hexane and the 80:20 mixture of *n*-hexane and methyl tertiary-butyl ether were equivalent to Freon 113 for petroleum-contaminated samples. For the sonication extraction, only perchloroethylene in non-petroleum

samples was equivalent to Freon 113 (Soxhlet results).

He then presented two graphs (Exhibits 14 and 15 of the June 1993 report) showing the RMSD results for each of the alternative techniques evaluated in the study. For non-petroleum samples, he noted that the (Varian) SPE column using *n*-hexane or 80:20 was equivalent to Freon 113 (using separatory funnel). He cautioned, however, that that result was based only on five samples and should be viewed with caution. The (3M) 90 mm SPE disk using Freon 113 gave equivalent results to Freon 113 with a separatory funnel. For petroleum-contaminated samples, he noted that none of the alternative techniques were equivalent to Freon 113.

Mr. Litow concluded with a chart that summarized the solvents that yielded results equivalent to Freon 113 for the separatory funnel, Soxhlet extraction and sonication techniques. Perchloroethylene was equivalent to Freon 113 twice, *n*-hexane twice, and 80:20 once. *Mr. Litow's presentation materials may be found in Appendix C.*

#### **Question and Answer Period**

Question: A member of the audience asked if there were any theories to explain the difference between water and solid matrices, relative to influencing the TSS (total suspended solids)?

Answer: Mr. Telliard replied that there was as yet no satisfactory explanation.

Mr. Telliard then briefly described some experimental work with solid phase extraction (SPE) cartridges done in the EPA Region III Central Regional Laboratory. He introduced the next speaker, Mr. Rex Hawley, who had cooperated with and furthered those studies.

#### **Evaluation of Solid Phase Extraction Columns for Analysis of Oil and Grease in Aqueous Samples: *Rex Hawley, Varian Sample Preparation Products***

The first speaker on SPE was Rex Hawley of Varian Sample Preparation Products. He described work done with SPE cartridges that were improved on the basis of problems encountered during Region III's work. Mr. Hawley stressed simplicity, error reduction, low cost, and rapidity, as well as reduced solvent usage as advantages of using SPE. Mr. Hawley presented the apparatus used in Varian's work, including both common laboratory apparatus and specialized components. He outlined the basic procedure used to prepare the equipment and analyze a sample. He discussed an evaluation of filter materials and a technique to remove water from the eluent without using sodium sulfate (an Aquasep filter.) He presented the results of tests run with Varian's SPE cartridges on synthetic standard samples (Mazzola oil in deionized water) versus the results obtained by the EPA separatory funnel method, and indicated that good agreement was obtained. Comparable results were also obtained for samples collected by the Los Angeles County Water District. Mr. Hawley then discussed the results of analyses of samples provided by EPA. Some of these samples were difficult to analyze because of high solids contents, which caused long elution times. This problem was circumvented by the use

of several SPE columns per sample. Finally, Mr. Hawley discussed the distinction between extraction solvents in liquid/liquid extraction and elution solvents in SPE. *Mr. Hawley's presentation materials may be found in Appendix D.*

### Question and Answer Period

Mr. Telliard commented that SPE offers the advantage of being able to extract a sample in the field, and then ship it to a laboratory for elution and analysis.

Question: A member of the audience asked if the difference in recoveries among the various elution solvents could be due to differences in the materials extracted by the solvents (using SPE).

Answer: Mr. Hawley replied that within the SPE results, there were no great differences among the results for various solvents. He also stressed that the results would be different for a particular solvent used with liquid-liquid extraction versus SPE, because the principles of the two techniques are different. In SPE, the solid phase media does the extraction, and the solvents merely elutes extracted material off the SPE cartridge. Mr. Telliard reinforced this point by stating that the variability in the SPE method comes from the solubility of the extracted material in the elution solvent, rather than from the extraction by the SPE medium.

Question: A member of the audience asked if the final determination was done gravimetrically.

Answer: Mr. Hawley answered that it was.

Question: A member of the audience asked if the boiling point of the elution solvent made any difference in the results.

Answer: Mr. Hawley answered that the elutropic properties of the solvent, not the boiling point, are what matter.

Question: A member of the audience asked if the fact that the boiling points of some of the materials measured are lower than those of the solvents tested makes any difference to the results.

Answer: Mr. Hawley said that it did not, because oil and grease is defined in the method as materials boiling over 70 °C.

Mr. Telliard commented that the two samples that were the topic of the preceding questions, one from a leather tannery and one from a railroad yard timber treating area, were challenging samples for which inconsistent results might be expected.

Question: A member of the audience asked about the capacity of the SPE column (in terms of weight retained).

**Answer:** Mr. Hawley replied that the capacity of the columns tested, which have a five-gram bed of SPE material, could be as high as 1,000 mg, and that since the sample bottle is still connected to the system when the elution is done, that oil and grease retained on the walls of the bottle would also be eluted.

**Question:** A member of the audience asked how the volume of solvent used to elute the SPE column was chosen, given the question of the column capacity.

**Answer:** Mr. Hawley answered that he had conducted experiments that showed that one 20 mL aliquot and one 10 mL aliquot of elution solvent were sufficient to elute all but one or two mg of oil and grease.

**Question:** A member of the audience asked a question about having a second cartridge in the SPE experimental apparatus.

**Answer:** Mr. Hawley explained that for samples with large amounts of particulates, the SPE cartridge may become clogged. When this happens, the sample bottle may be separated from the apparatus, righted, a new cartridge attached, and the extraction restarted.

**Question:** Mr. Telliard asked if both SPE cartridges were then eluted.

**Answer:** Mr. Hawley replied that they both were eluted.

Mr. Telliard commented that the ability to use multiple cartridges offered flexibility when extracting samples with high oil and grease contents.

**Question:** A member of the audience asked for more information on the use of the AquaSep column in the experimental apparatus to remove water.

**Answer:** Mr. Hawley described the position of the AquaSep column as being below the SPE column, which allows the eluting solvent, but not water, to drip through to the collection box.

### **Oil and Grease Analysis in Wastewater Using Solid Phase Extraction Disks: *Craig Markell, The 3M Corporation***

The third speaker on SPE was Craig Markell of the 3M Corporation, who discussed work done with their 47mm and 90mm SPE disks. He began by reviewing the principles of solid phase extraction in comparison to liquid/liquid extraction. Next he showed some photographs of the SPE disks, including a micrograph of the spherical SPE material. He described the efficiency of the SPE disks by showing a picture of a disk which had been used to extract an orange dye from water. He then showed some pictures of a six-place manifold with a process controller used for multiple extractions.

Mr. Markell presented some information on types of compounds that may be extracted with SPE, noting that substances with water solubilities up to about 1/10 of 1% could be

extracted. He noted that higher results will be obtained in the oil and grease test when compounds that may be neutral or ionic (such as phenol) are in their protonated (neutral) form, as at pH 2. He also noted that high salt concentrations (ionic strength) in the sample will change the partition coefficient and result in greater extraction. Mr. Markell then discussed the capacity of SPE devices, stating that capacity is greater for hydrophobic compounds and smaller for water-soluble compounds.

He then outlined the method used with the SPE disks including sample sizes, elution times and solvent aliquot volumes, and the drying step using sodium sulfate. Sodium sulfate was eliminated from the sample using a syringe-end filter. He presented a diagram of an SPE disk in its holder with the filter aid material on top. He explained that a filter aid such as glass beads was useful to avoid overloading the SPE disk, especially if the sample contained free-phase oil. He presented results for five solvents on a number of different samples, showing that generally higher results were obtained with more polar solvents (he contrasted this result with what Mr. Hawley had said earlier about the elution solvent not making a difference in the results). Mr. Markell then presented results of the analysis of some of the Phase I study samples, showing general correlations for two groups of high and low concentration samples. He presented precision data for the SPE disk method, which ranged from 0 to 23% difference. He concluded by saying that, while nothing will duplicate Method 413.1 (the EPA oil and grease method using Freon 113 and a separatory funnel) exactly, SPE disks do work for oil and grease. *Mr. Markell's presentation materials may be found in Appendix E.*

#### Question and Answer Period

Question: A member of the audience asked if Mr. Markell had any data on the effect of sample salinity on SPE extraction.

Answer: Mr. Markell replied that he did not have any such data for the oil and grease method, but work he had done on more polar analytes such as phenol confirms the "salting out" effect for neutral compounds and also shows the expected lower recoveries for ionic compounds due to higher ionic strength.

Question: The same questioner asked for clarification of Mr. Markell's answer in terms of the function of the C18 packing.

Answer: Mr. Markell answered that salt changes the partition coefficient of water in contact with the bonded phase (C18 packing.)

Question: The same questioner expressed doubt that the partition coefficient was as important in SPE as in liquid-liquid extraction.

Answer: Mr. Markell suggested that they talk about this issue in more detail later.

Mr. Telliard noted that the questioner was referring to "produced water" which has a high salt content, and that high salt content did not interfere with extraction of organic compounds, as was shown in the study report.

Mr. Telliard then introduced the next speaker, William Eckel of DynCorp Viar.

**Evaluation of Oil and Grease Samples using NDIR and Flon S-316: *William Eckel, DynCorp Viar, Inc.***

Mr. Eckel described the use of the Horiba OCMA 220 nondispersive infrared (NDIR) analyzer for determination of oil and grease using a modification of EPA Method 413.2. A proprietary solvent, Flon S-316, that was originally used in a continuous on-line process monitor where a high boiling point was required, is used in the OCMA 220. Horiba used this instrument to analyze 38 samples collected during Phase I of the study. Mr. Eckel stated that the Horiba instrument extracts 15 mL of sample with 15 mL of solvent, and measures the absorbance at 2930 reciprocal centimeters without evaporating the solvent. He said that this should lead to higher results than are obtained with Method 413.1, because the lower-boiling oils are not boiled away with the solvent. Mr. Eckel described the Horiba instrument as a non-dispersive infrared analyzer, meaning it does not scan wavelengths. He stated that, of all the solvents tested in the study, only perchloroethylene could also be used in the Horiba instrument, since that solvent contains no hydrogen and therefore has no carbon-hydrogen stretch in its IR spectrum. (Perchloroethylene was not tested in Phase I by Horiba, however.)

He then showed results of analyses for Phase I study samples. He began with Exhibit 10 from the June 1993 report, which indicated that the Horiba results were 60% higher than Freon 113 overall, 20% higher for petroleum-based samples, and over twice as high for non-petroleum samples. He noted that the RMSD results showed that the Horiba results were not equivalent to Freon 113 and then described difficulties with the extraction of some of the more challenging samples. Emulsion-free extractions were obtained by shaking samples with solvent in 40 mL VOA vials.

Results for 38 samples showed that 17 results were higher than the Freon 113 separatory funnel method, 17 were lower, and four were below 5 mg/L by both methods. Mr. Eckel then displayed Exhibits 14 and 15 of the June 1993 report to show how the Horiba analyzer compared to the other alternative techniques for non-petroleum samples and petroleum samples, respectively. Finally, he showed Exhibit 16 which showed the mean solvent-to-Freon ratios for all of the alternative techniques including Horiba.

Mr. Eckel concluded that, because of their increased sensitivity and reduced solvent usage, infrared techniques would continue to be considered for the determination of oil and grease. *Mr. Eckel's presentation materials may be found in Appendix F.*

**Question and Answer Period.**

**Question:** A member of the audience asked if the performance of Freon 113 in the Horiba analyzer had been tested and compared to Flon.

**Answer:** Mr. Eckel replied that Horiba had not used Freon 113 to analyze any of the Phase



I study samples. He further noted that all alternative techniques in the study were compared to the results obtained with Freon 113 and EPA Method 413.1 (separatory funnel or Soxhlet extraction and gravimetric determination).

Mr. Telliard commented that Horiba also offers a solvent reclamation system to recover the Flon solvent.

**Question:** A member of the audience asked if there was any problem obtaining a representative 15 mL sample from a liter of water that is inherently a two-phase system of oil and water.

**Answer:** Mr. Telliard answered that while he believed analysis of the entire one-liter sample would be more representative, he had no data to prove it. He indicated that the issue of sample representativeness (including the issue of grab samples) would be addressed in Phase II of the study.

**Question:** A member of the audience asked if the Horiba instrument had been tested with prepared standards, rather than just collected samples.

**Answer:** Mr. Telliard replied that the manufacturer had analyzed standard samples. He also noted that the SPE and infrared techniques discussed were for aqueous samples only.

Mr. Telliard then introduced the next speaker, Gerald DeMenna of Chem-Chek Consulting/Buck Scientific.

**Determination of Oil and Grease by Evaporation of Solvent in a Quartz Cell in an Infra-red Spectrophotometer: *Gerald DeMenna, Chem-Chek Consulting/ Buck Scientific***

Mr. DeMenna began by describing the difficulties his laboratory has had in obtaining good results with the oil and grease test using a variety of techniques and solvents. He then described a procedure developed in his laboratory that is designed to yield results similar to the EPA gravimetric method now in use. The new method uses the same sampling and extraction methodology as before, but uses infrared spectroscopy to make the final determination. A new quartz evaporation plate/infrared cell was developed specifically for this use. In the proposed procedure, smaller amounts of sample (100 mL versus one liter) and solvent are used in the extraction. Mr. DeMenna asserted that good correlation with tests run with a full liter of sample is obtained when using only 100 mL of sample. A thin film of oil and grease is cast by evaporation of an aliquot of the extract in the quartz plate and this is placed in the open sample compartment of an infrared analyzer.

Comparative analyses were performed between the quartz plate evaporation technique, a normal liquid quartz cell technique (similar to EPA Method 413.2) and Method 413.1. For the liquid cell technique, extractions are carried out in screw-cap cells used for GC headspace analysis to avoid evaporation. These filled cells are placed in the beam of the IR analyzer and the hydrocarbon materials are measured as absorbance, transmission units or directly in parts

per million. For the new evaporation technique, the final gravimetric determination of Method 413.1 has been replaced by measurement in a high signal-to-noise infrared photometer. These three techniques were compared using a standard mixture of isooctane, hexadecane and chlorobenzene.

The evaporation plate technique has the advantage of using far less solvent. Mr. DeMenna discussed the construction of the quartz IR evaporation plate and the method of pipetting the sample into it. A 250 uL portion of the extract is pipetted into a quartz plate with a 300 uL cavity. The solvent is evaporated away at  $75 \pm 2$  °C on the heat fins of the infrared analyzer, and the absorbance of oil and grease measured at 3.4 microns (2950 wave numbers). Infrared analyzers with closed cells or flow cells are not amenable to the new technique.

Mr. DeMenna presented some results from environmental samples taken in northeastern states, comparing the EPA gravimetric method (413.1), his new quartz plate/evaporation method and the quartz liquid cell technique (413.2.) All techniques were performed with Freon 113. His results showed that his new quartz evaporation plate method gave slightly higher results than the EPA gravimetric method, and slightly lower than the quartz liquid cell method. Precision was comparable for the three methods, and spike recoveries were good.

He described an experiment performed after a similar workshop was held in Norfolk, Va. on May 4, 1993. The purpose of this experiment was to compare Freon 113 and methylene chloride. Results with methylene chloride on a brackish water sample were 30 to 50% higher than with Freon 113.

Mr. DeMenna then discussed the detection limit and linear range of the IR quartz evaporation plate technique. The detection limit at 0.004 absorbance units was 1.5 ppm, and response was linear to 250 ppm.

He concluded by saying that the new technique offers higher throughput in the laboratory, reduced solvent usage, and is adaptable to any IR instrument with an open sample compartment. *Mr. DeMenna's presentation materials may be found in Appendix G.*

#### Question and Answer Period

Question: A member of the audience asked if Mr. DeMenna had any problems with the oil and grease residue running out of the cavity in the quartz plate after evaporating the solvent.

Answer: Mr. DeMenna answered that residues of up to 500 ppm isooctane, hexadecane and chlorobenzene did not present any such problems.

Question: A member of the audience asked if there had been any problems with bumping when boiling off the solvent.

Answer: Mr. DeMenna answered that no boiling was involved in the work he had done. The solvent was evaporated away by placing the quartz plate on the heat fins of the IR instrument. He also mentioned some experiments he had done that showed

that no residual solvent was left after 60 seconds of evaporation.

**Strategy Options for Regulating Oil and Grease: William A. Telliard, U.S. EPA Office of Science and Technology**

Mr. Telliard then discussed the policy options being considered at EPA to resolve the problem of Freon 113 use in the oil and grease method. He noted that the Canadian government was also studying this problem, and that they, as well as he, were leaning toward *n*-hexane as the replacement solvent. He explained that *n*-hexane was originally an alternative solvent to Freon 113 in the standard method, but was later dropped. He stated that generally lower results are obtained with *n*-hexane than with Freon 113, so that switching to *n*-hexane should not cause (NPDES) permit holders to become noncompliant.

Mr. Telliard recalled that the issue of *n*-hexane's neurotoxicity had been raised at the Norfolk workshop, so that he intended to investigate the applicability of cyclohexane to both gravimetric and solid phase extraction techniques in Phase II of the study.

He then discussed the other alternative solvents. He stated that perchloroethylene would be retained in the study, because results equivalent to Freon 113 were obtained for some solid samples with sonication and because it could be used with infrared techniques. Turning to the 80:20 mixture of *n*-hexane and methyl tertiary-butyl ether, he stated that, contrary to what his slide said, he had decided to drop further consideration of that solvent. He cited laboratory safety and solvent storage (evaporation resulting in a ratio other than 80:20) considerations as his reasons. Methylene chloride would be dropped, he said, since it had produced no results equivalent to Freon 113. He also said that DuPont 123 would be dropped since it is a Class II chlorofluorocarbon scheduled for phase-out, and because it had positive results in some mutagenicity tests.

Mr. Telliard stated that he wanted to continue to investigate solid phase extraction and infrared techniques.

He then turned to a discussion of policy options. The first option he presented was to do away with the oil and grease method. This was suggested often by commenters. He noted that while this was still a viable option, it would not be easy to implement.

He also mentioned the possibility of modifying the method by adding cleanup procedures that would provide more definitive separation of polar and nonpolar materials. He stated that this option would be considered in Phase II.

The third option he presented was to obtain a waiver under the Clean Air Act Amendments of 1990 to allow continued use of Freon 113 for this purpose. He noted, however, that with the approaching ban on Freon 113, and its high cost, this was not a viable option.

The fourth option he presented was to develop a correction factor to correct results for an alternative solvent to what would have been obtained using Freon 113. He stated that this could take the form of demonstrating the performance of a given solvent, and then reverting to that solvent at the time of permit renewal. He mentioned that this approach would be in line with the current concept of "performance-based" methods.

The fifth option was for EPA to select one solvent or extraction technique that produces results closest to Freon 113. At this point, the likely choice would be *n*-hexane or cyclohexane with some cleanup steps.

The sixth option was to select more than one solvent, since some solvents work better with petroleum-based materials and others with non-petroleum-based materials. Mr. Telliard noted that additional data would be needed to support such a decision, and that there was not sufficient time to collect it before a decision needed to be made.

The seventh option presented was to give further consideration to alternative techniques, such as gas chromatography (GC) and infrared. He noted that the Office of Water had used the petroleum hydrocarbons method (using GC) for the Offshore Oil and Gas Industry and Petroleum Refining Industry studies, and that IR was a widely used screening tool. He raised the issues of comparability between methods and the higher cost of these other measurements as issues to be overcome. He stated that this might be the most technically sound option, but that it would be difficult to revise the many regulations and permits that are based on gravimetric data. He said that more than one technique could be chosen, in line with the Agency's performance-based methods approach.

Mr. Telliard again noted that the Canadians were leaning toward *n*-hexane. He said EPA was focusing on *n*-hexane or cyclohexane, and solid phase extraction. He stated that if there were truly no significant change in regulatory monitoring results (NPDES testing for oil and grease) by going to the alternative solvent, that a correction factor would not be needed. He qualified this by saying that EPA would have to state that a switch to the leading solvent would mean less strict regulation than with Freon 113. *Mr. Telliard's presentation materials may be found in Appendix H.*

Mr. Telliard then opened the floor for questions and discussion.

#### Question and Answer Period

Question: Mr. Hawley asked if pentane was being considered, as suggested at the Norfolk Workshop.

Answer: Mr. Telliard answered that it was not, due to laboratory safety issues (as with petroleum ether, of which pentane is the predominant component.) Mr. Litow added that its boiling point was also an issue, since it boils at room temperature at high altitudes.

- Question:** A member of the audience asked if supercritical fluid extraction (SFE) was being examined for solid samples.
- Answer:** Mr. Telliard replied that an Office of Solid Waste workgroup was studying SFE, and that a subgroup of the workgroup was looking at SFE for elution in solid phase extraction (SPE.) He noted that all of the solvents have their drawbacks, and that SFE would be a nice way to go if it were commercially available.
- Question:** A member of the audience recounted his experience of switching away from gravimetric to an infrared method, and asked why a new solvent rather than an alternative method such as IR was being contemplated.
- Answer:** Mr. Telliard answered that his immediate mandate was to solve the issue of the gravimetric method, and to do it by December.
- Question:** A member of the audience commented that compliance monitoring will be problematic when there is a local limit across many industrial categories, and a new solvent measures different substances than before, depending on what is in the wastewater. Another comment related to the previous question, and asserted that infrared methods would give results more than 10% higher than gravimetric methods. Finally, it was asserted that substances that are not oil nor grease cause positive oil and grease results using the present methods.
- Answer:** Mr. Telliard answered that the method name "oil and grease" is a misnomer, since what the method actually measures is what comes out of the solvent. He commented that the oil industry is concerned that the method measures sulfur and other non-oil substances. He repeated that the ultimate answer may be to replace the oil and grease method, but that the issue at hand was to replace Freon 113.
- Question:** A member of the audience asked if performance-based methods would be the best way to establish an infrared method.
- Answer:** Mr. Telliard replied that it would be, but cautioned that the comparability of the methods was not established, and it would be expensive to do so.
- Question:** A member of the audience asked if laboratories would continue to be urged to reclaim their solvent after the solvent change had been made.
- Answer:** Mr. Telliard replied that they would.
- Question:** The same questioner stated that solvent recovery would be more difficult with hexane.
- Answer:** Mr. Telliard agreed.
- Question:** A member of the audience asked what the timing and content of Phase II of the study would be.
- Answer:** Mr. Telliard answered that it would start in a couple of weeks, and that it would involve the solvents he had mentioned as being retained in the study as well as solid phase extraction. He qualified this by saying that having a Phase II

depended on obtaining funding, and that if time and money did not permit, then the decision would be to go with hexane. He noted that because of the mandate to do away with Freon 113, a proposed decision would have to go out for comment by the end of the year, and would have to go final by early spring.

**Question:** A member of the audience asked how many rules (effluent guidelines) there were for which oil and grease was limited.

**Answer:** Mr. Telliard replied that guidelines limit oil and grease discharges for 25 industries.

**Question:** The same questioner asked if not regulating oil and grease would cause "backsliding" if other parameters also control the same pollutants.

**Answer:** Mr. Telliard answered that it probably would not, since many guidelines also contain limitations on other conventional parameters such as BOD (biological oxygen demand) and TSS (total suspended solids).

**Question:** A member of the audience asked if his industry could propose substituting an alternative method, such as petroleum hydrocarbons by gas chromatography, if the results could be shown to be reproducible and comparable to the Freon 113 method.

**Answer:** Mr. Telliard replied that this was possible, but that it would be difficult to prove that the methods were "equivalent", since they are known to measure different substances. He noted that the issue of an alternative measurement in lieu of oil and grease was still on the table.

**Question:** The same questioner asked how to approach EPA with a question of method equivalency.

**Answer:** Mr. Telliard replied that a "bridging package" involving the Assistant Administrator for Water, the Office of Science and Technology, the Permits Division and Enforcement Division and others would need to be put together to advance such an issue.

**Question:** The same questioner asked if performance-based standards would be the way to advance an alternative technique.

**Answer:** Mr. Telliard replied that it would. He qualified this by saying that it appears that performance-based methods will require meeting detection limits and method specifications, and as the present oil and grease method has no specifications, there is nothing to which to compare a new method. He indicated that after a new solvent is chosen, a method detection limit study and a round robin study would be performed to establish method specifications. Also, solvent comparability to Freon 113 will be studied to avoid "accidental noncompliance" with permit requirements due to the use of the new solvent.

**Question:** A member of the audience stated that the oil and grease method is why they are

- in "accidental noncompliance."
- Answer:** Mr. Telliard corrected himself and said there is no such thing as "accidental noncompliance."
- Question:** A member of the audience asked how a solvent substitution would work in terms of permit limits and compliance.
- Answer:** Mr. Telliard explained that if the substitute (not equivalent) solvent produced results greater than Freon 113 does, there would be a permit compliance issue. If the substitute solvent always gives results lower than Freon 113, then EPA could change the solvent via the Federal Register notice and comment process, and all permit numbers would stay the same. At the time of permit renewal, the new solvent could be factored in, based on the data the permittee had been collecting using the new solvent. Another option would be to have every permittee develop a correction factor based on measurements of the same samples with Freon 113 and the new solvent and use the correction factor to amend the permit. He allowed that implementing the solvent change in terms of permits would be difficult, and that EPA was going to have to find the most cost-effective way to do it.
- Question:** A member of the audience asked if research on alternative methods would continue beyond the December deadline for choosing the substitute solvent.
- Answer:** Mr. Telliard replied that he hoped to eventually do away with the oil and grease measurement, and allow it to be replaced by another technique or techniques. He cautioned that further research was resource-dependent, and that the priority of actions was to find a substitute solvent, determine whether a correction factor is needed, and then look at how to phase out the oil and grease test. He added that, at the same time, it was necessary to avoid any "technical" noncompliances.
- Question:** A member of the audience asked what the purpose of the oil and grease test was.
- Answer:** Mr. Telliard replied that it was a continuation of sanitary engineering practice related to primary Publicly Owned Treatment Works (POTWs).
- Question:** A member of the audience asked why a "calibrated eyeball" test could not be used for sheen detection.
- Answer:** Mr. Telliard answered that he had made the suggestion to regulate by using a sheen number, and requiring further testing if that number is exceeded. He also mentioned that immunoassay test kits could be used to do screening, and EPA was looking into that.
- Question:** A member of the audience asked whether there would be a time period in which a method to replace oil and grease would be integrated into the standard methods.
- Answer:** Mr. Telliard replied in the affirmative.
- Question:** The same questioner asked if implementation of a new method would have to be

contingent upon review of categorical standards and local regulations involving different industries. If so, would the new method not simply be substituted for oil and grease.

Answer: Mr. Telliard answered that it would not.

Question: The same questioner asked whether regulations would have to be changed because of a different measurement method.

Answer: Mr. Telliard answered that they would.

Question: The questioner expressed concern about how this would be interpreted in the regulated community.

Answer: Mr. Telliard replied that that was why this meeting was being held in Boston, namely, to allow the industries in Region I that had been sampled to express their views.

Mr. Telliard closed the workshop by thanking the attendees for coming, and asked them to provide him with any other comments or information they might have to share before the anticipated time of the decision on the oil and grease method.



**Appendix A**  
**Workshop Agenda**



**OIL AND GREASE WORKSHOP  
WEDNESDAY JUNE 30, 1993**

**Agenda**

**Chairman:** William A. Telliard

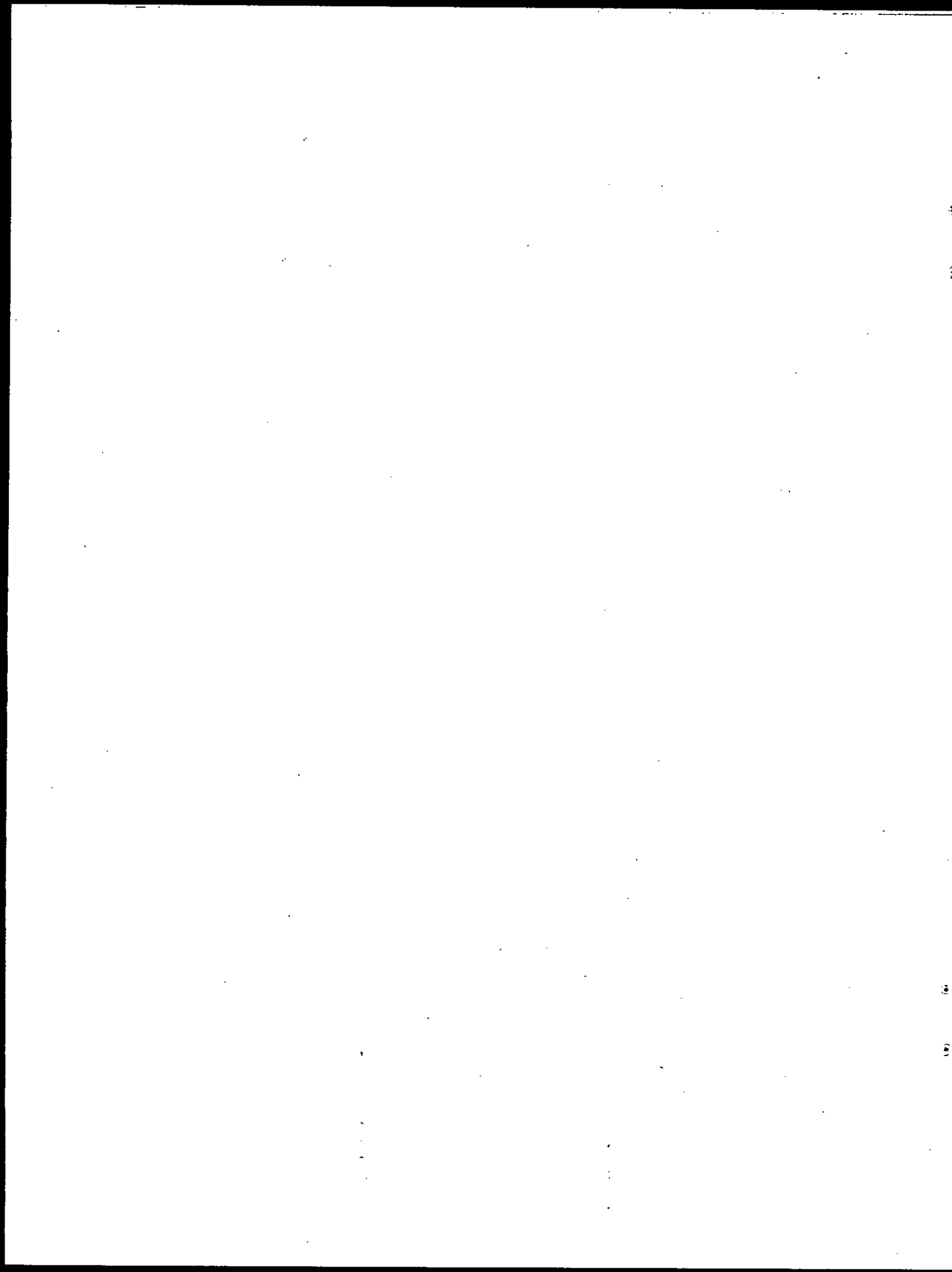
- 1:00 - 1:15 Welcome and Introduction
- 1:15 - 1:45 Freon Replacement Study, Phase I Study Results  
*William A. Telliard, U.S. EPA Office of Science and Technology*
- 1:45 - 2:00 Data Evaluation and Statistics, Phase I Study Results  
*Roger Litow, DynCorp Viar, Inc.*

**Solid-Phase Extraction**

- 2:00 - 2:15 EPA Region III Analysis Using Solid Phase Extraction Columns  
*William A. Telliard, U.S. EPA Office of Science and Technology*
- 2:15 - 2:30 Evaluation of Solid Phase Extraction Columns for Analysis of Oil and Grease in Aqueous Samples  
*Rex Hawley, Varian Sample Preparation Products*
- 2:30 - 2:45 Oil and Grease Analysis in Wastewater Using Solid Phase Extraction Disks  
*Craig Markell, The 3M Corporation*
- 2:45 - 3:00 Break

**Infra-Red**

- 3:00 - 3:15 Oil and Grease Samples using NDIR and Flon S-316  
*William Eckel, DynCorp Viar, Inc.*
- 3:15 - 3:30 Determination of Oil and Grease by Evaporation of Solvent in a Quartz Cell in an Infra-red Spectrophotometer  
*Jerry DiMenna, Buck Scientific*
- 3:30 - 4:15 Open Discussion
- 4:15 - 4:30 Closing Remarks

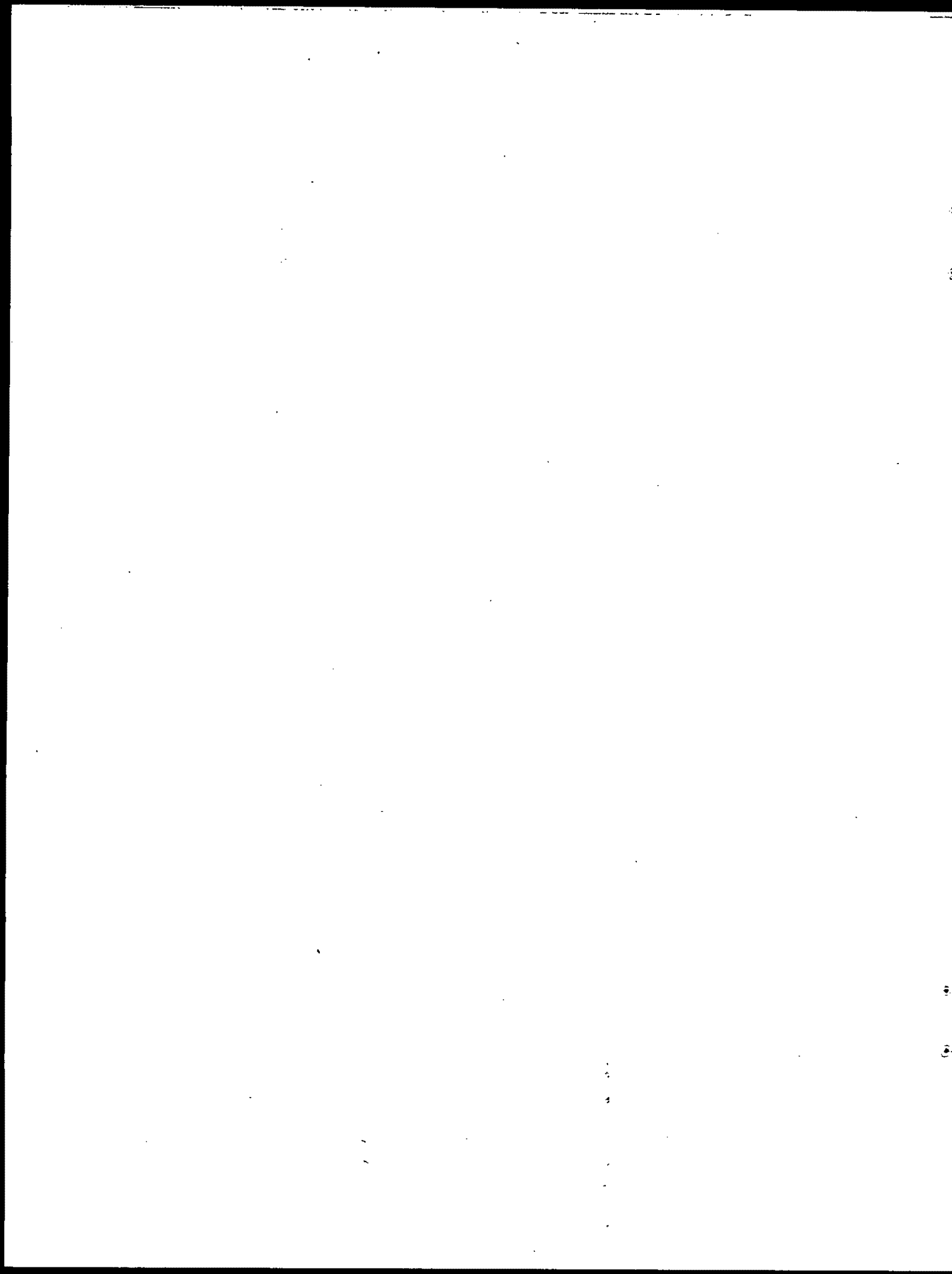


**Appendix B**

**Presentation Materials**

**"Freon Replacement Study, Phase I Study Design"**

**William A. Telliard, U.S. EPA Office of Water**



# **EPA Efforts to Replace Freon-113 for the Determination of Oil and Grease**

C51-001-010

# **Regulatory History**

- Montreal Protocol on Substances that Deplete the Ozone Layer regulates the use of chlorofluorocarbons (CFCs), with an eventual phase out by 1996.



# "Oil and Grease" is a Method-Defined Parameter: Depends on Solvent Used

# **Study Plan: Phase I**

- Find a solvent (if any) that gives results equivalent to Freon-113, or
- Select Solvent or Alternative Technique for Further Study

# **Candidate Solvents: Phase I**

- n-Hexane
- n-Hexane + MTBE (80/20)
- Methylene Chloride
- Perchloroethylene
- DuPont-123

# Oil and Grease is a Regulated Parameter for 10,500 NPDES Permits and 25 Effluent Guidelines Industries

# Using “Real World” Samples

---

- 39 plants
- 24 industrial categories
- 41 aqueous wastes
- 30 solid wastes

# **Alternative Techniques Being Tested**

---

- Solid Phase Extraction cartridges
- Solid Phase Extraction disks
- Infrared Technique

# **"Real World" Sample Types**

---

- Petroleum
- Animal Fats
- Vegetable Oils

# Treatment Systems at Plants Sampled are Effectively Removing Oil and Grease

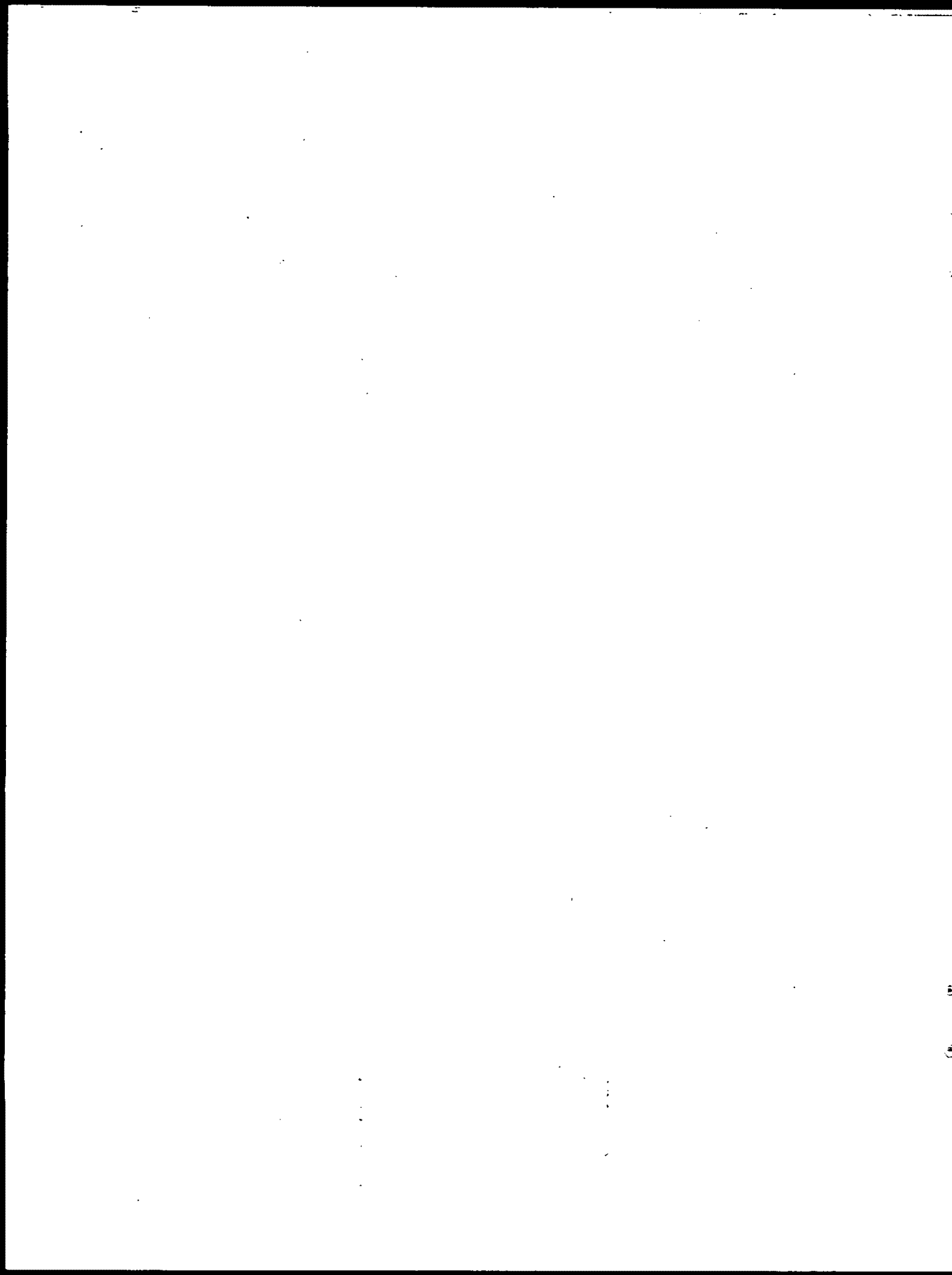


**Appendix C**

**Presentation Materials**

**"Freon Replacement Study, Phase I Study Results"**

**Roger Litow, DynCorp Viar, Inc.**



**A Mean Solvent to Freon Ratio Close to 1.00 Does  
Not Indicate That A Solvent Is Similar To Freon**

<b>Solvent</b>	<b>Sample 1</b>	<b>Sample 2</b>	<b>Mean</b>
A	0.90	0.96	0.93
B	0.50	1.50	1.00

**RMSD = Root Mean Square Deviation**

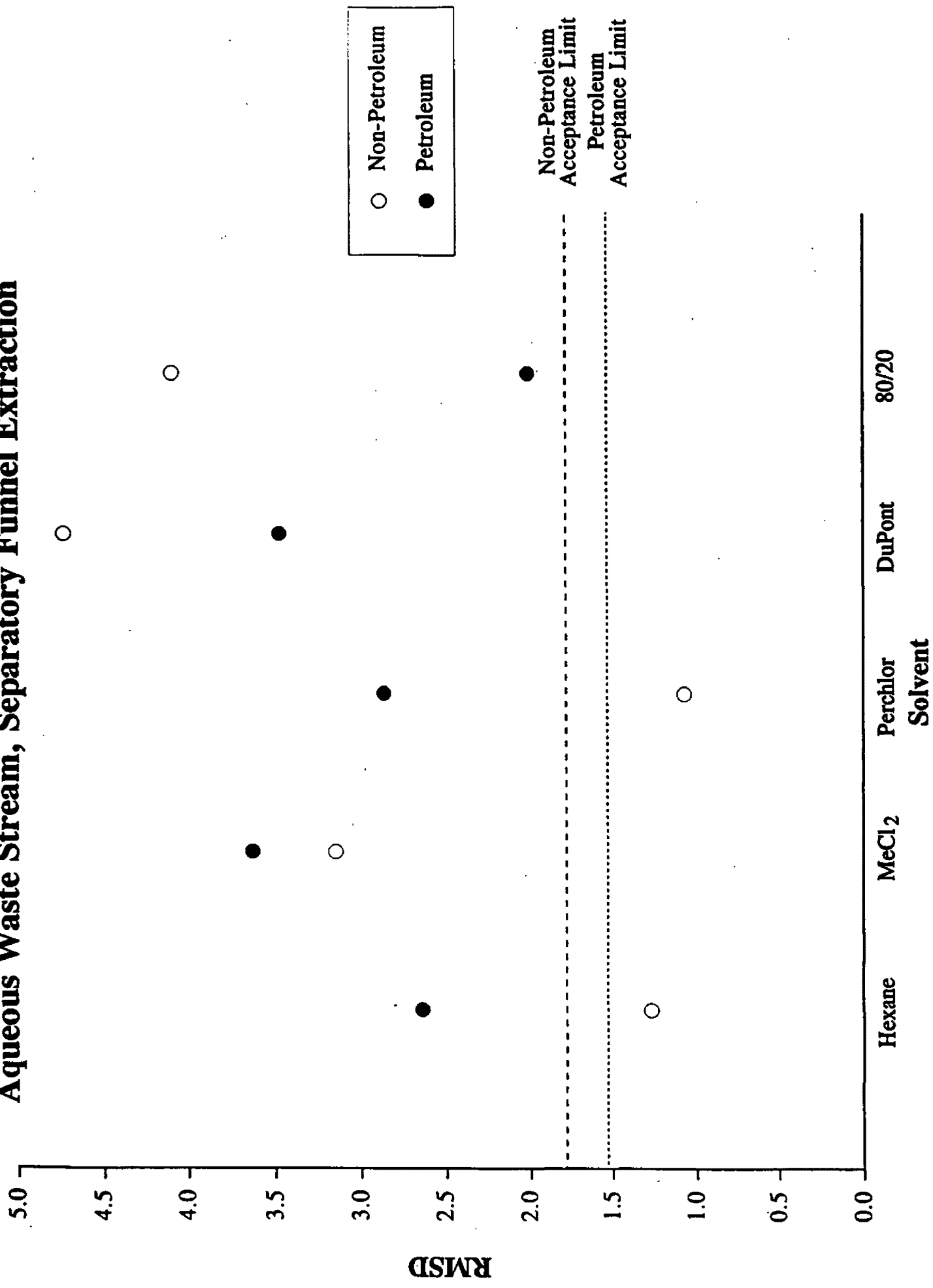
Deviation = O&G Extracted by Solvent - O&G Extracted by Freon

Square Deviation = (Deviation)<sup>2</sup>

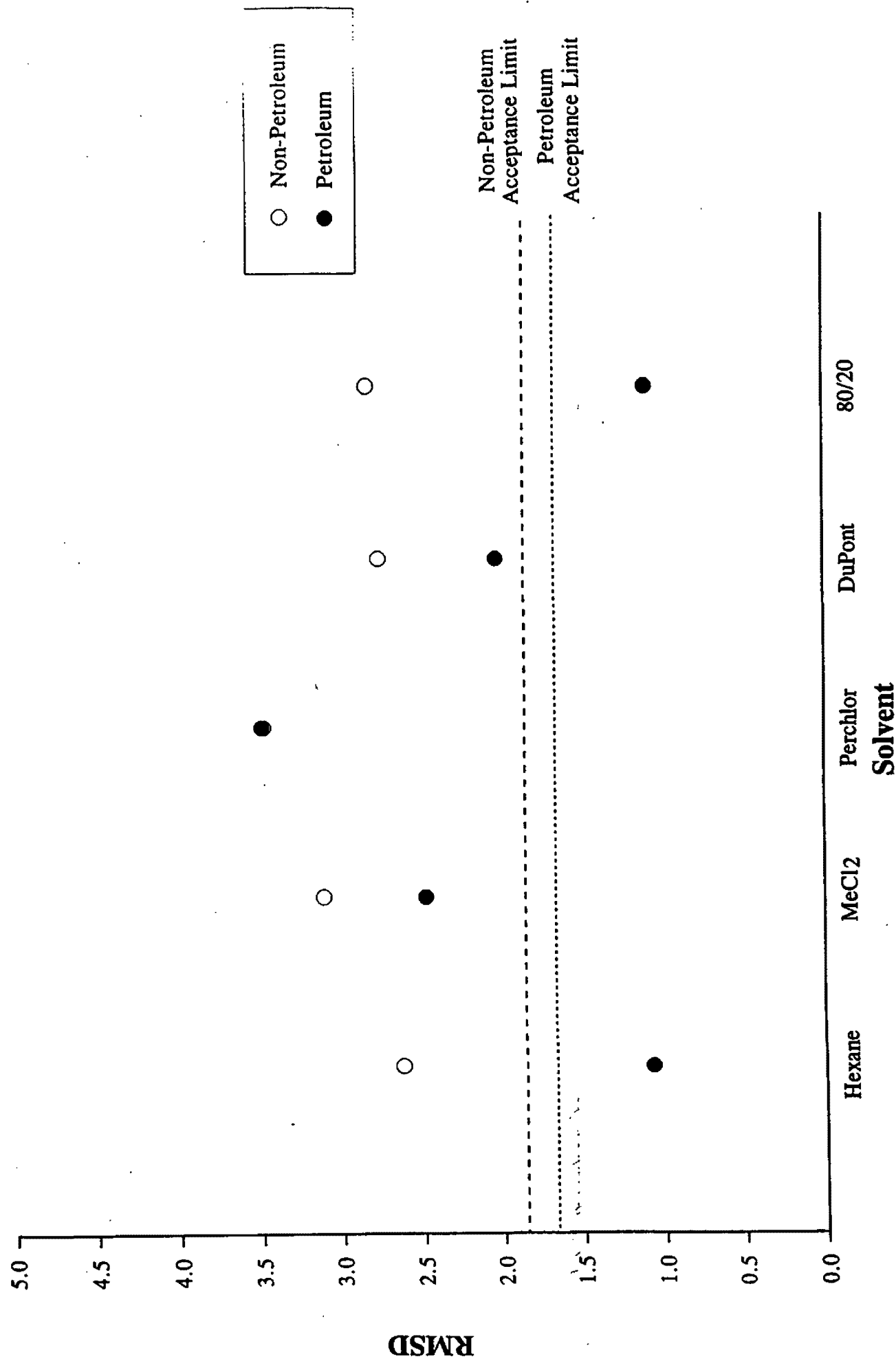
Mean Square Deviation = Square Deviation / number of samples

Root Mean Square Deviation = Square root of Mean Square Deviation

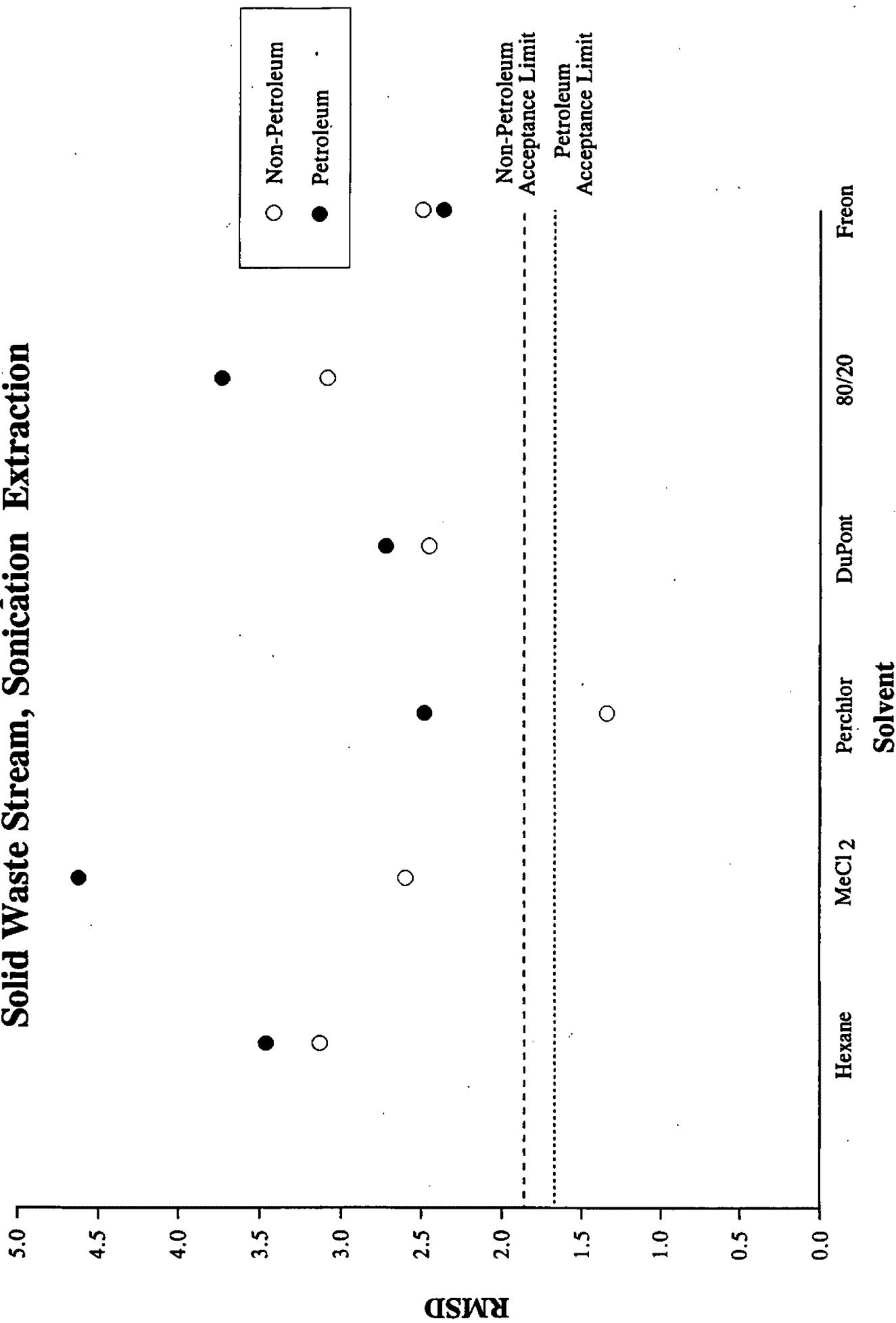
# Normalized Root Mean Square Deviations Aqueous Waste Stream, Separatory Funnel Extraction



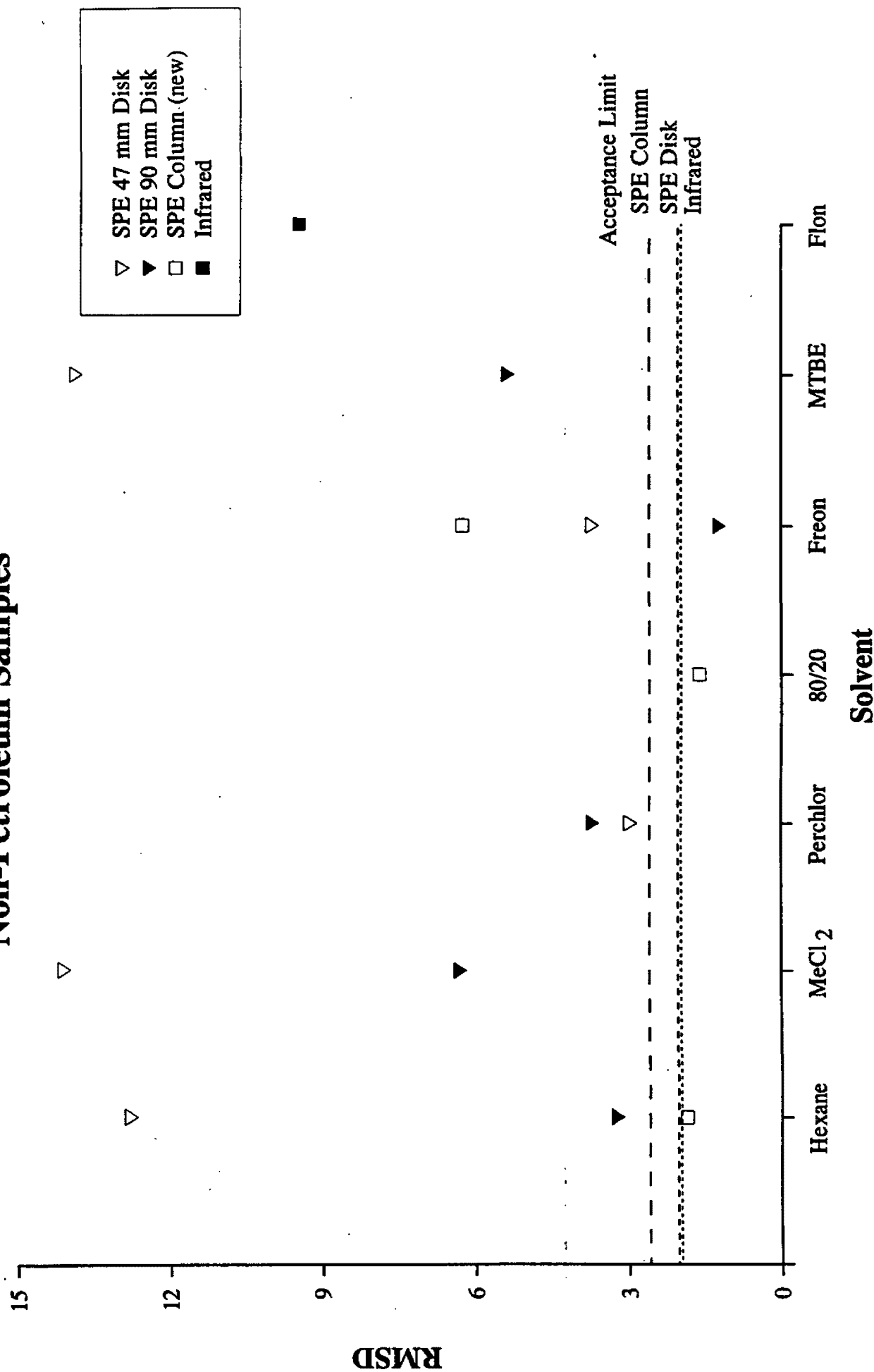
# Normalized Root Mean Square Deviations Solid Waste Stream, Soxhlet Extraction



# Normalized Root Mean Square Deviations Solid Waste Stream, Sonication Extraction

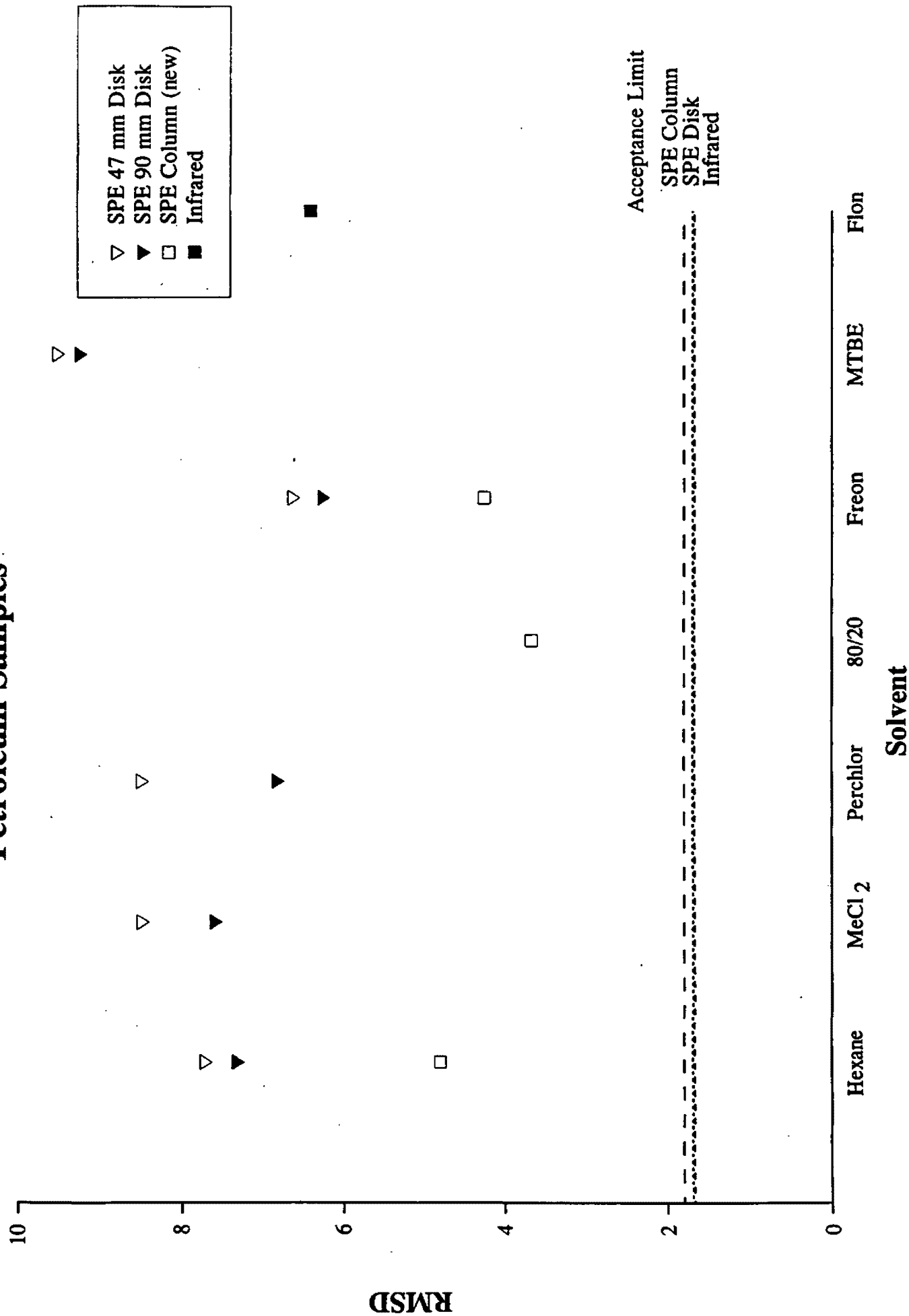


# Normalized Root Mean Square Deviations Aqueous Waste Stream, Alternative Techniques Non-Petroleum Samples





# Normalized Root Mean Square Deviations Aqueous Waste Stream, Alternative Techniques Petroleum Samples



# Solvents Which Do Not Differ From Freon 113

## By Matrix and Technique

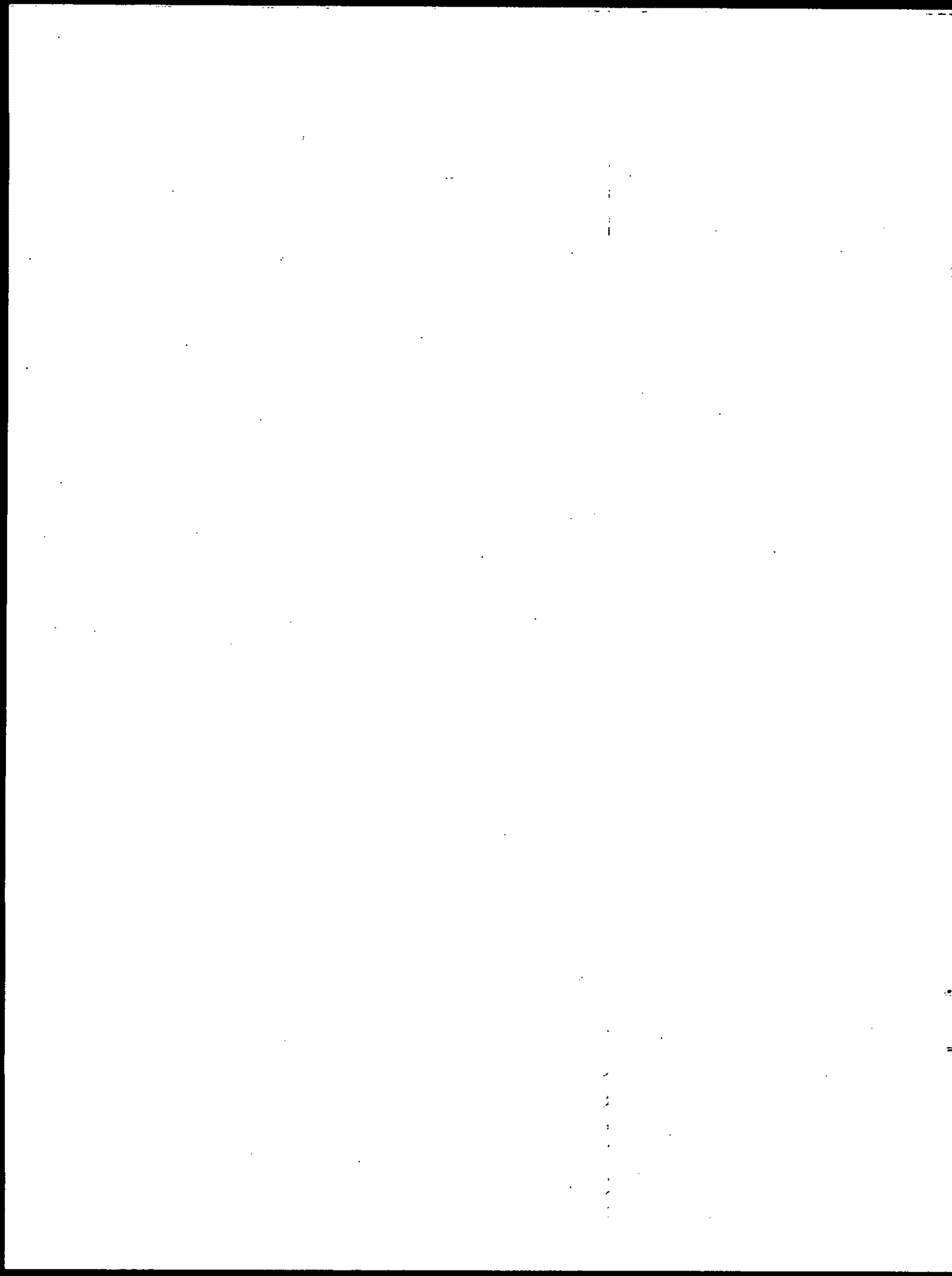
	All Samples	Non-Petroleum	Petroleum
Separatory Funnel		Hexane, Perchlor	
Soxhlet			Hexane, 80/20
Sonication		Perchlor	

## **Appendix D**

### **Presentation Materials**

#### **"Evaluation of Solid Phase Extraction Columns for Analysis of Oil and Grease in Aqueous Samples"**

**Rex Hawley, Varian Sample Preparation Products**



# Cost Effective

- ◆ Less expensive disposables
- ◆ Low solvent usage levels
- ◆ Less expensive solvent requirements
- ◆ Less labor intensive

# Error Reduction

- ◆ No sample transfers
- ◆ No emulsions
- ◆ Reduce clogging
- ◆ Can work with clogged cartridges
- ◆ Method blank  $\leq 1$  mg

# Simplicity

- ◆ Same Bottle/Cap for Sampling & Test
- ◆ No large separatory funnels
- ◆ Compact apparatus
- ◆ "Cook book" approach
- ◆ Simple analytical technique

# Common Laboratory Apparatus

- ◆ 89 mm wide mouth "1 liter" bottle
- ◆ 50 cc centrifuge tube
- ◆ Analytical (4 place) balance
- ◆ Solvents
- ◆ Dry down set up



# Unique Apparatus

- ◆ Processing station
- ◆ Adapter cap
- ◆ SPE cartridge
- ◆ Drying cartridge

# Basic Procedure

- ◆ Column rinse
- ◆ Column conditioning
- ◆ Sample extraction
- ◆ Water rinse
- ◆ Air dry
- ◆ Sample elution
- ◆ Dry down
- ◆ Analysis

# Filter Materials Evaluation

- ◆ Membrane
- ◆ Glass wool
- ◆ Glass beads
- ◆ Nylon packing

# Removal of Water from Sample

- ◆ Sodium Sulfate
- ◆ AquaSep

# Analyte Recovery

- ◆ Standards
- ◆ "Real world" samples

# Spiked Sample Recovery

Mazola Oil in Deionized Water

	Analyte (g)	% Recovery
1	1.0157	95
2	1.0299	92
3	0.9816	91
4	0.996	96
5	1.1332	88
6	0.9496	98
7	1.1195	93
8	1.0027	96
9	1.0557	91
Average Recovery =		93

Blanks less than 1 mg

# "Unknown" Comparative Study

using LCS and method blank

	SPE	LLE (Freon)
1	41.3	42.9
2	45.7	42.3
3	45.2	43.3
4	41.4	45.5
5	48.2	46
6	44	43.7
Average=	44.3	44

Blanks less than 1 mg

# Spiked Sample Comparative Study

## Vegetable Oil in Deionized Water

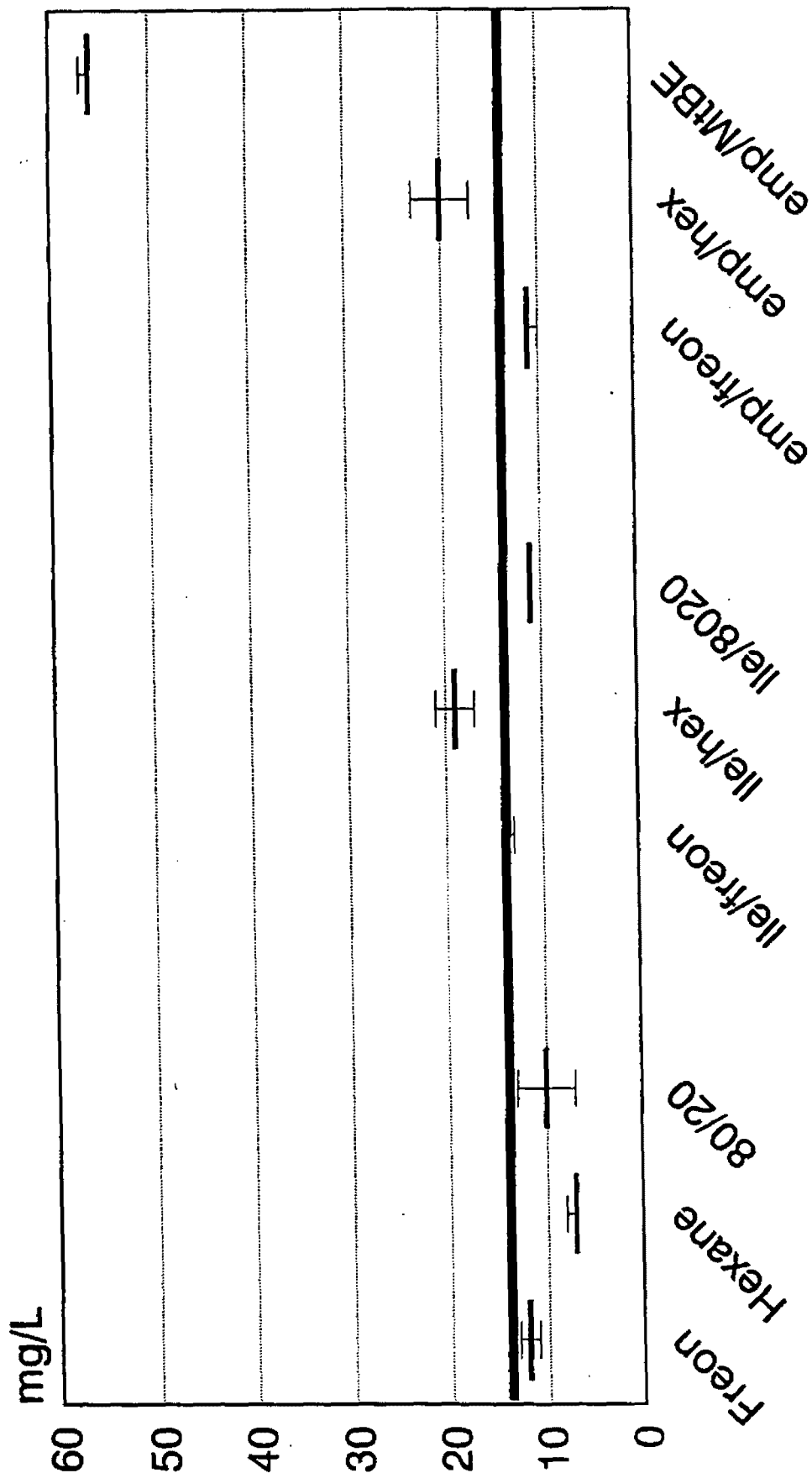
Method	% Recovery	Std. Dev.
LLE	99.9	1.8
CLLE	97.8	0.6
SPE	94.1	5.3

Blank adjusted



# Seafood Plant

Primary Effluent #23121

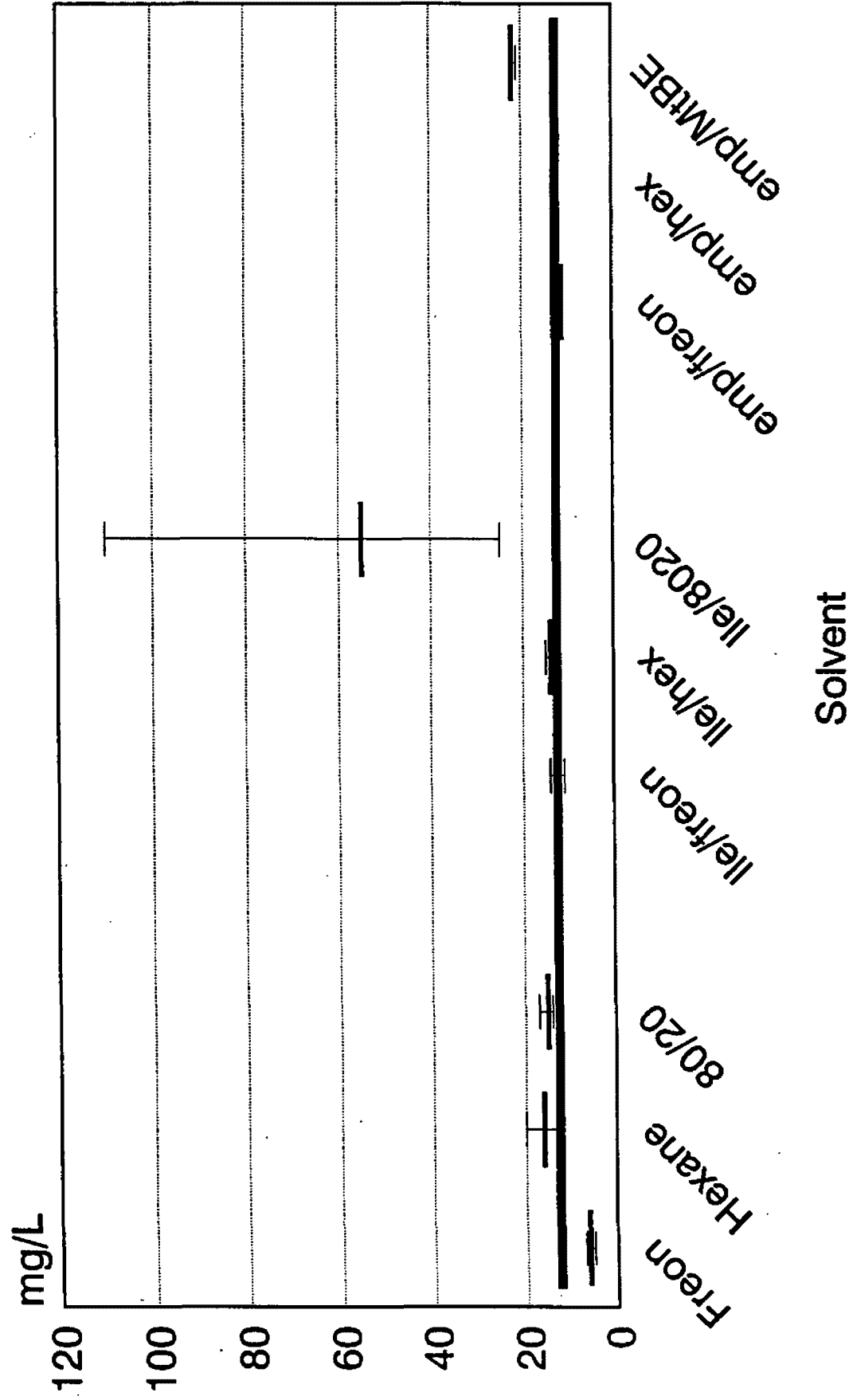


Solvent

Flow rate=38 min/L

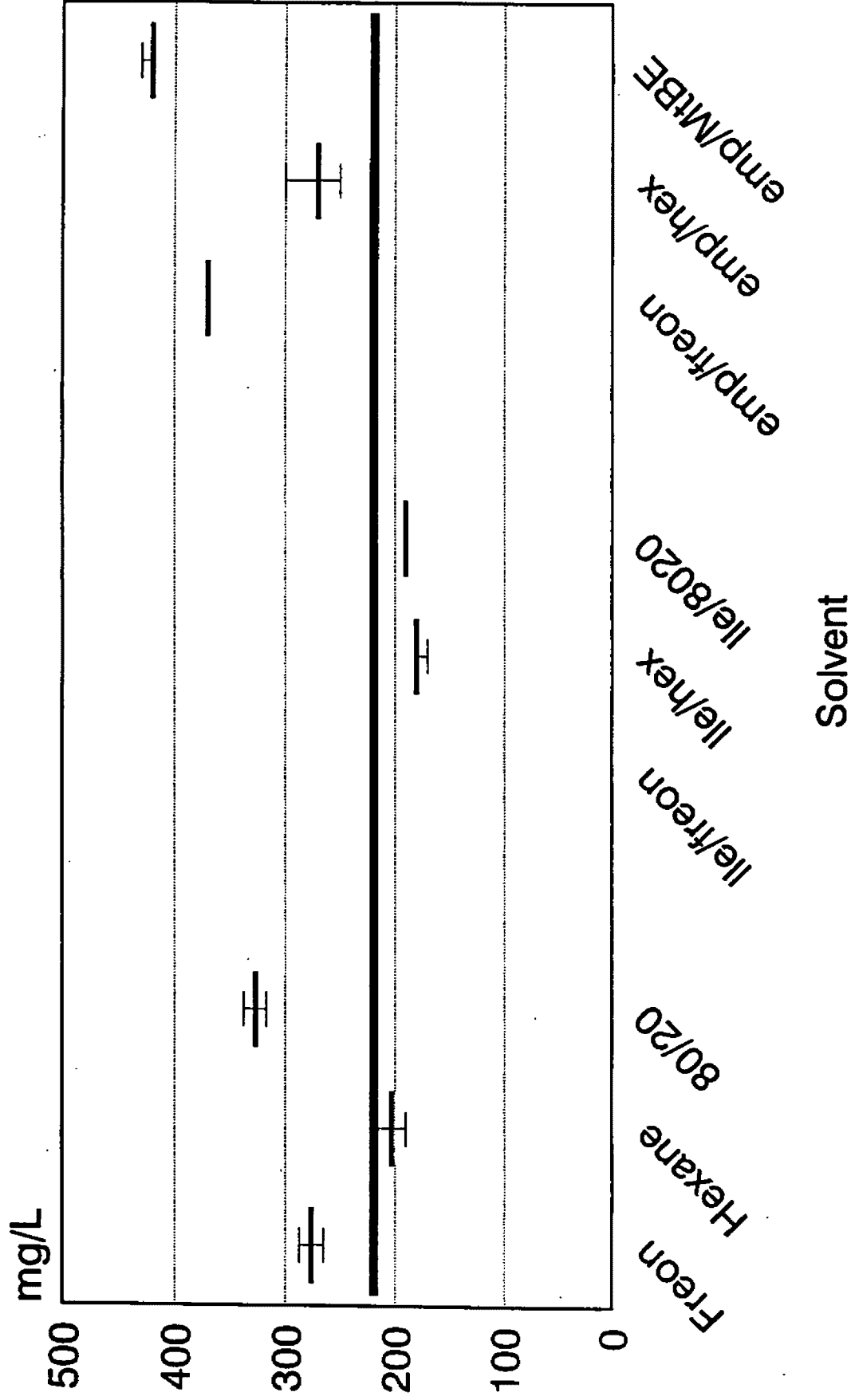
# Meat Packing Plant

Lagoon Effluent #23124



# Can Manufacturing Plant

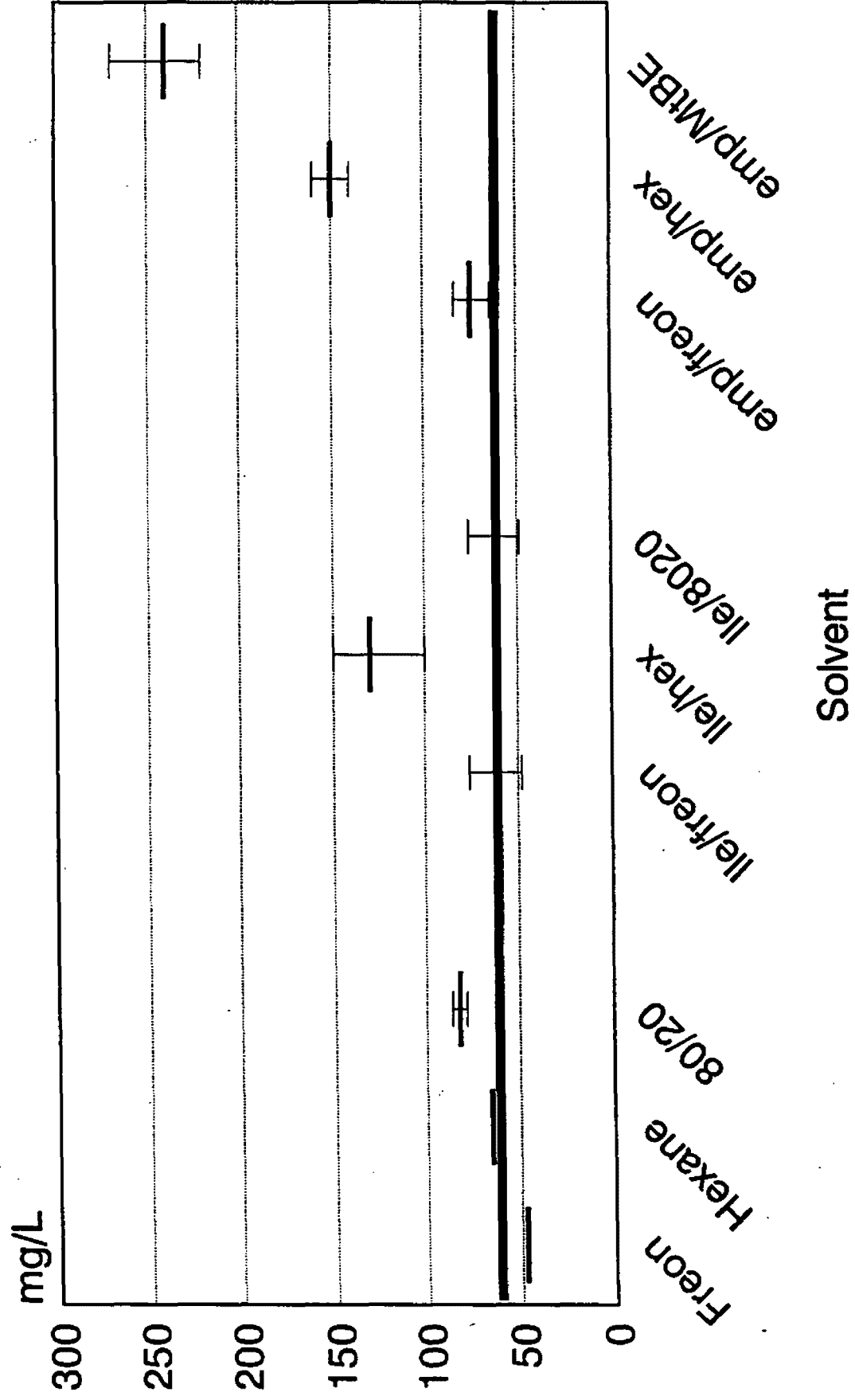
Primary Effluent #23461



Flow rate=16 min/L

# Leather Tannery

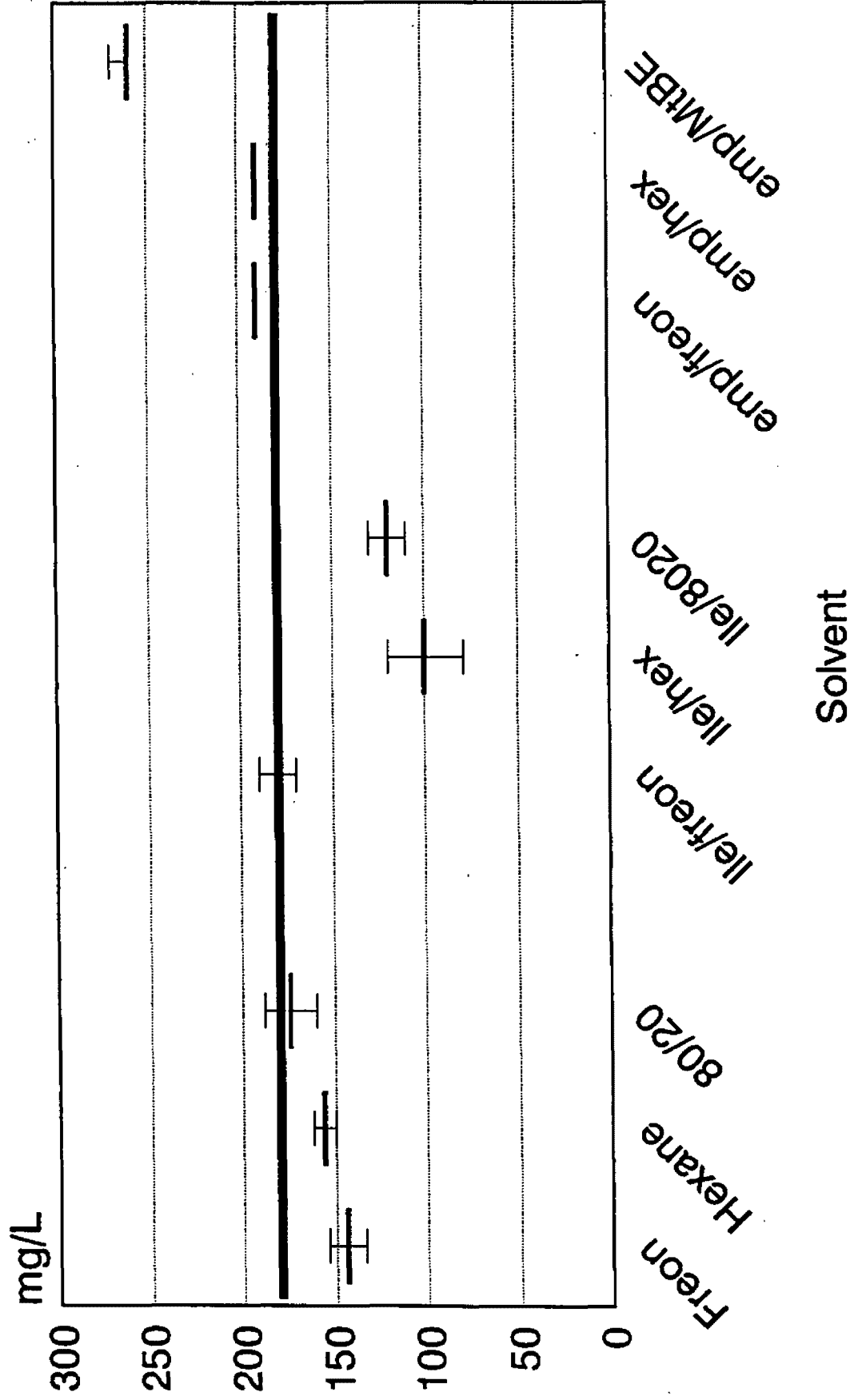
Primary Effluent #23482



Flow rate=503 min/L

# Industrial Laundry

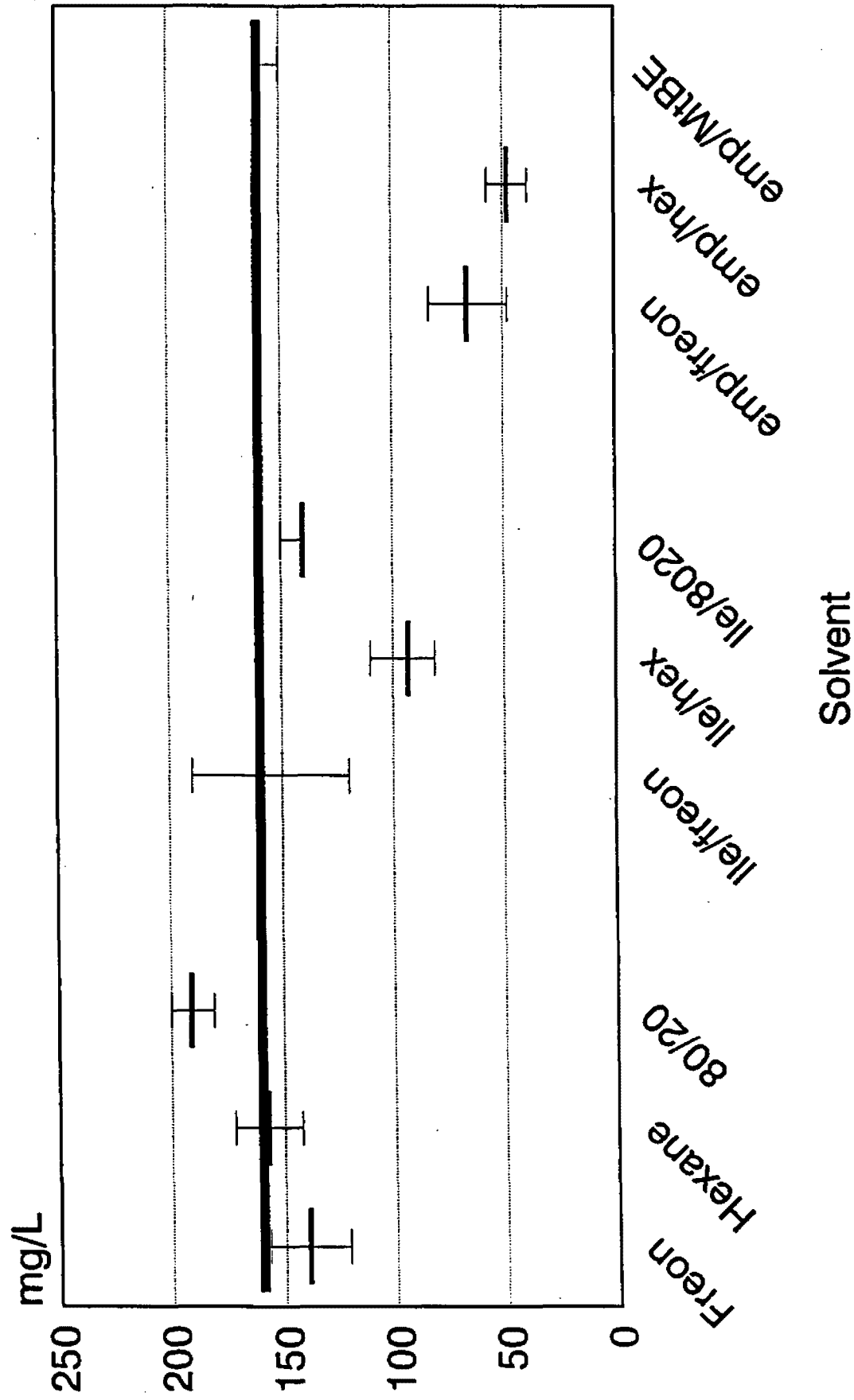
Primary Effluent #23480



Flow rate=13 min/L

# Railroad Yard

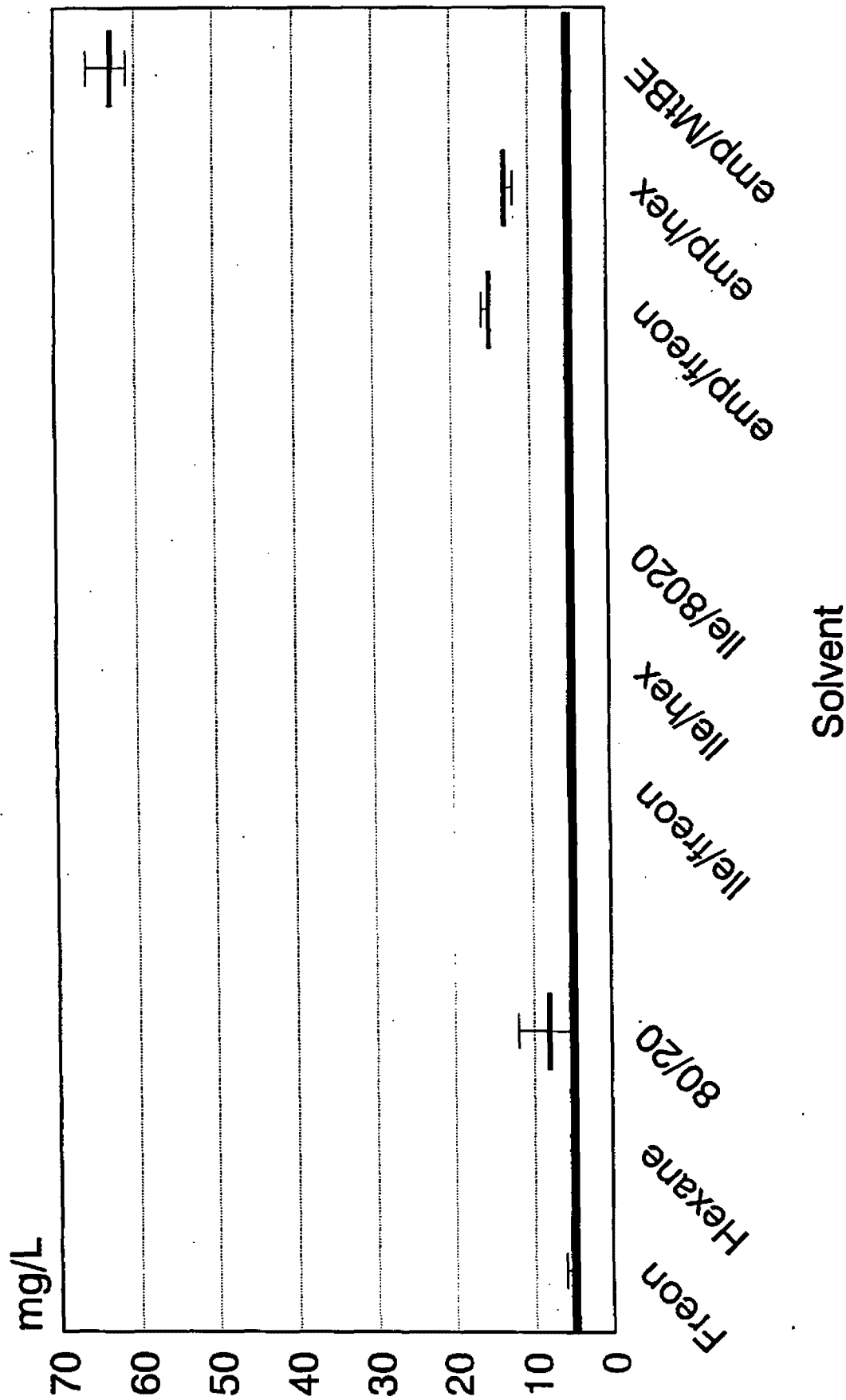
DAF Effluent #23459



Flow rate = 254 min/L

# Paper Mill

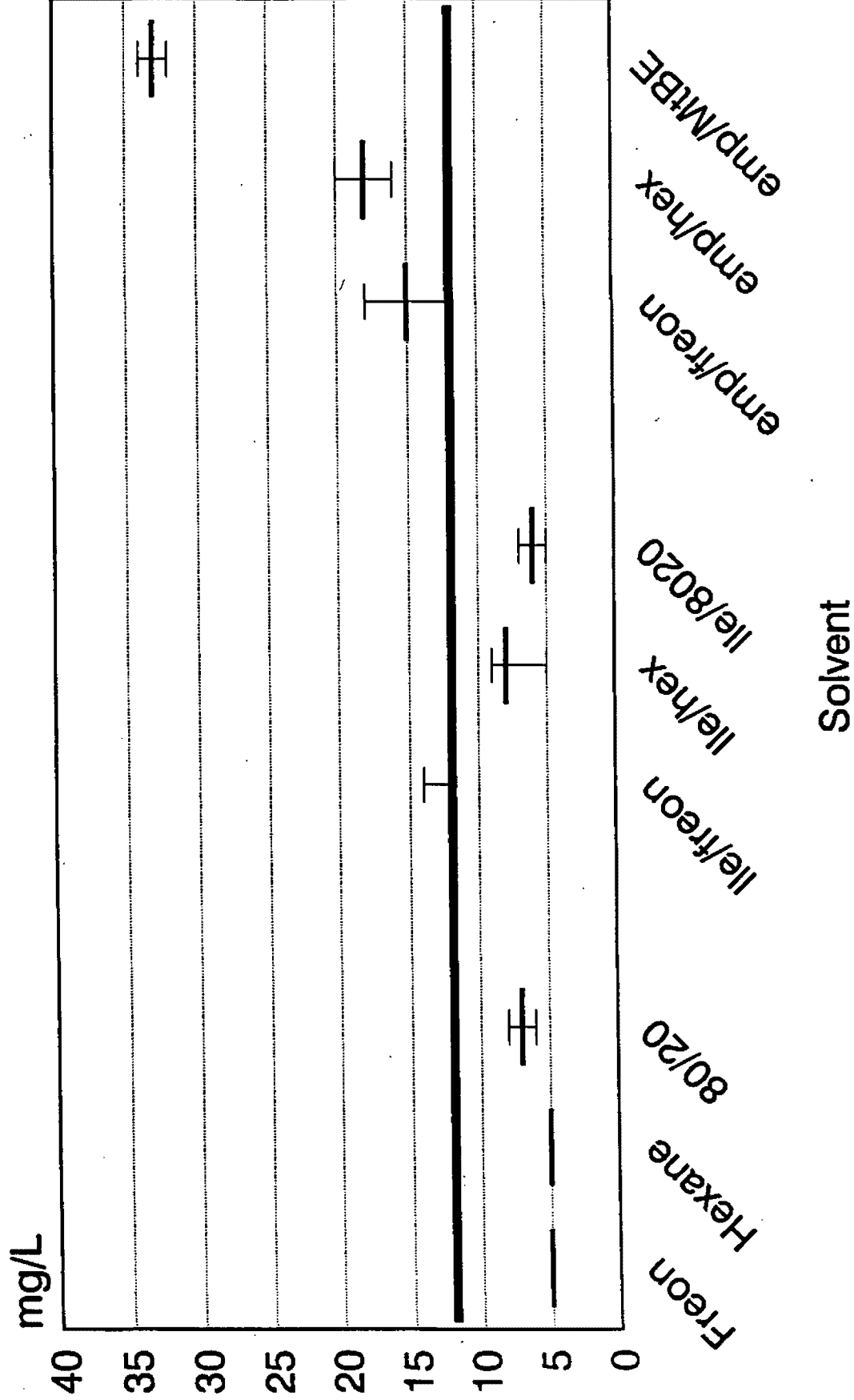
Bleach Plant Effluent #23479



Flow rate=19 min/L

# Petroleum Refinery

Interceptor Effluent #23485

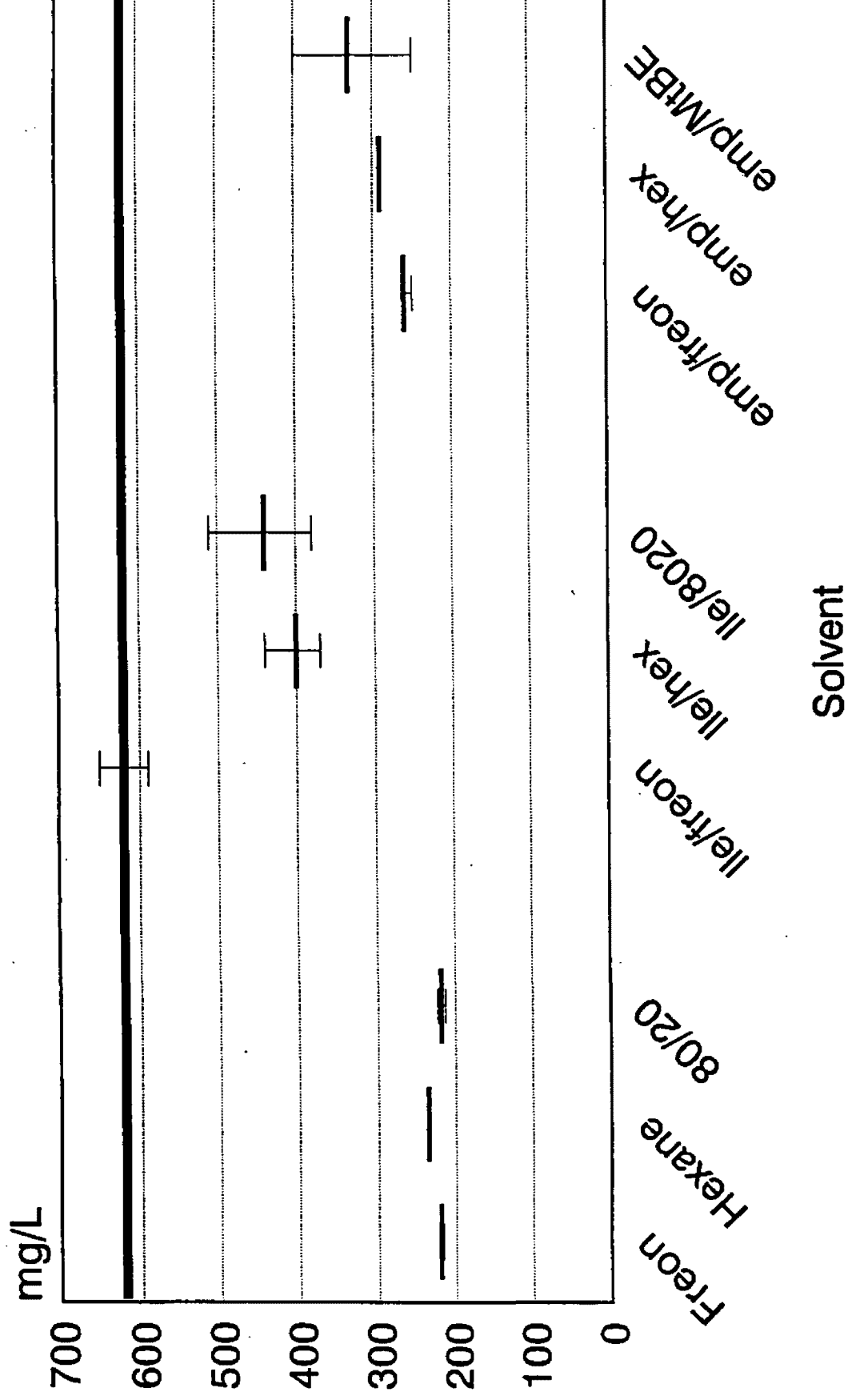


Flow rate=20



# Industrial Laundry

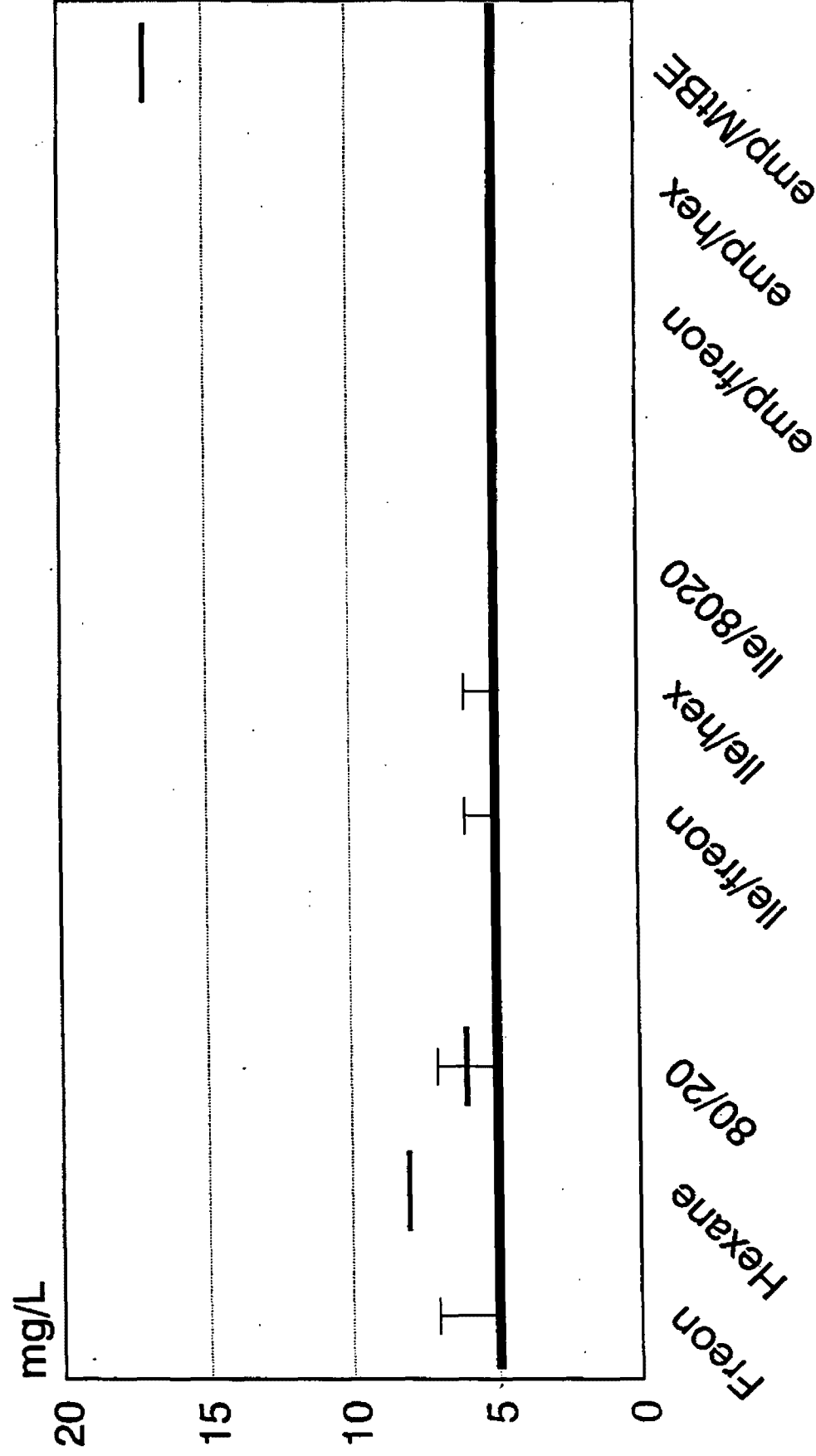
DAF Effluent #23463



Flow rate=37 min/L

# Oil Terminal

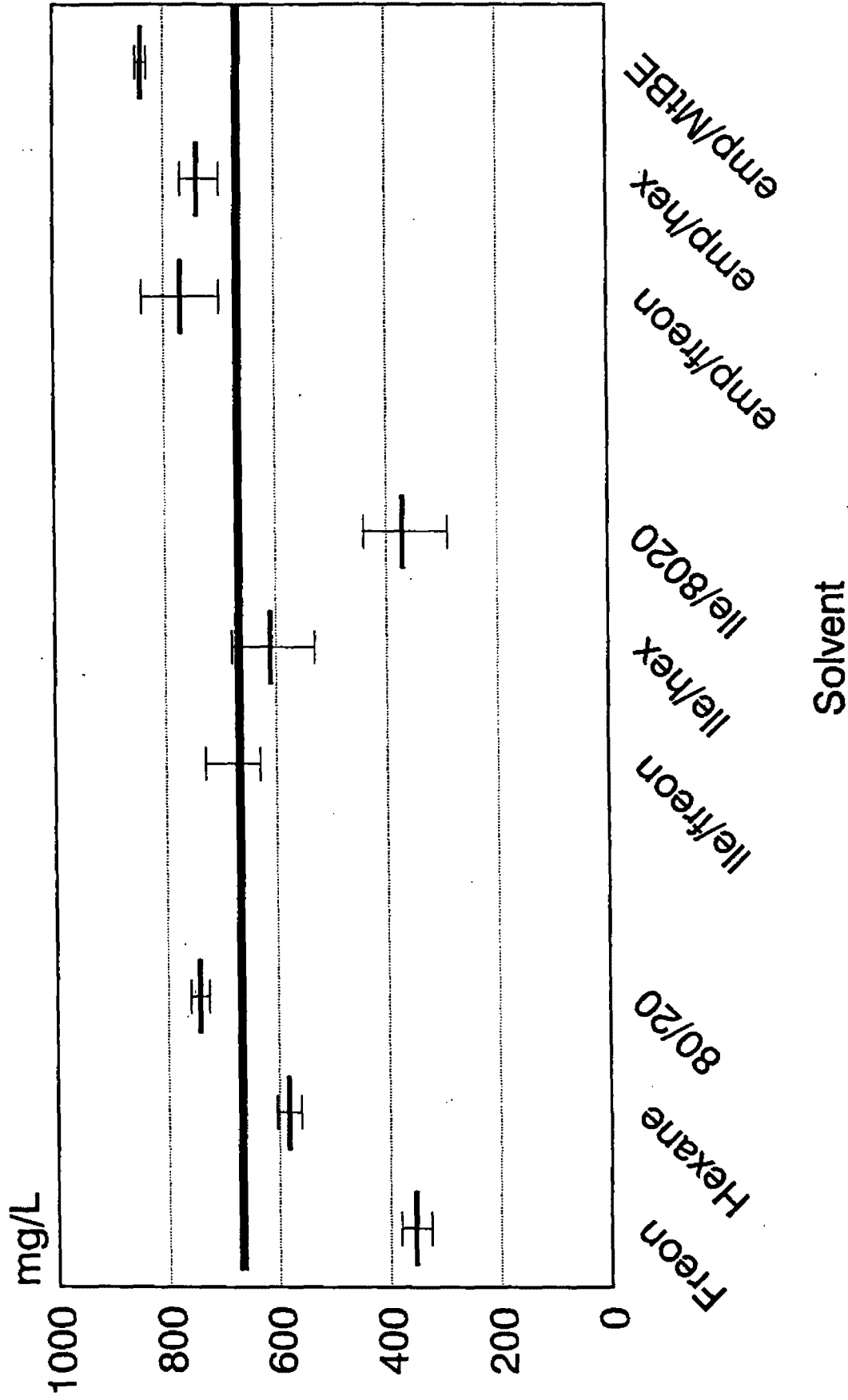
Separator Effluent #23120



Flow rate=15 min/L

# Poultry Plant

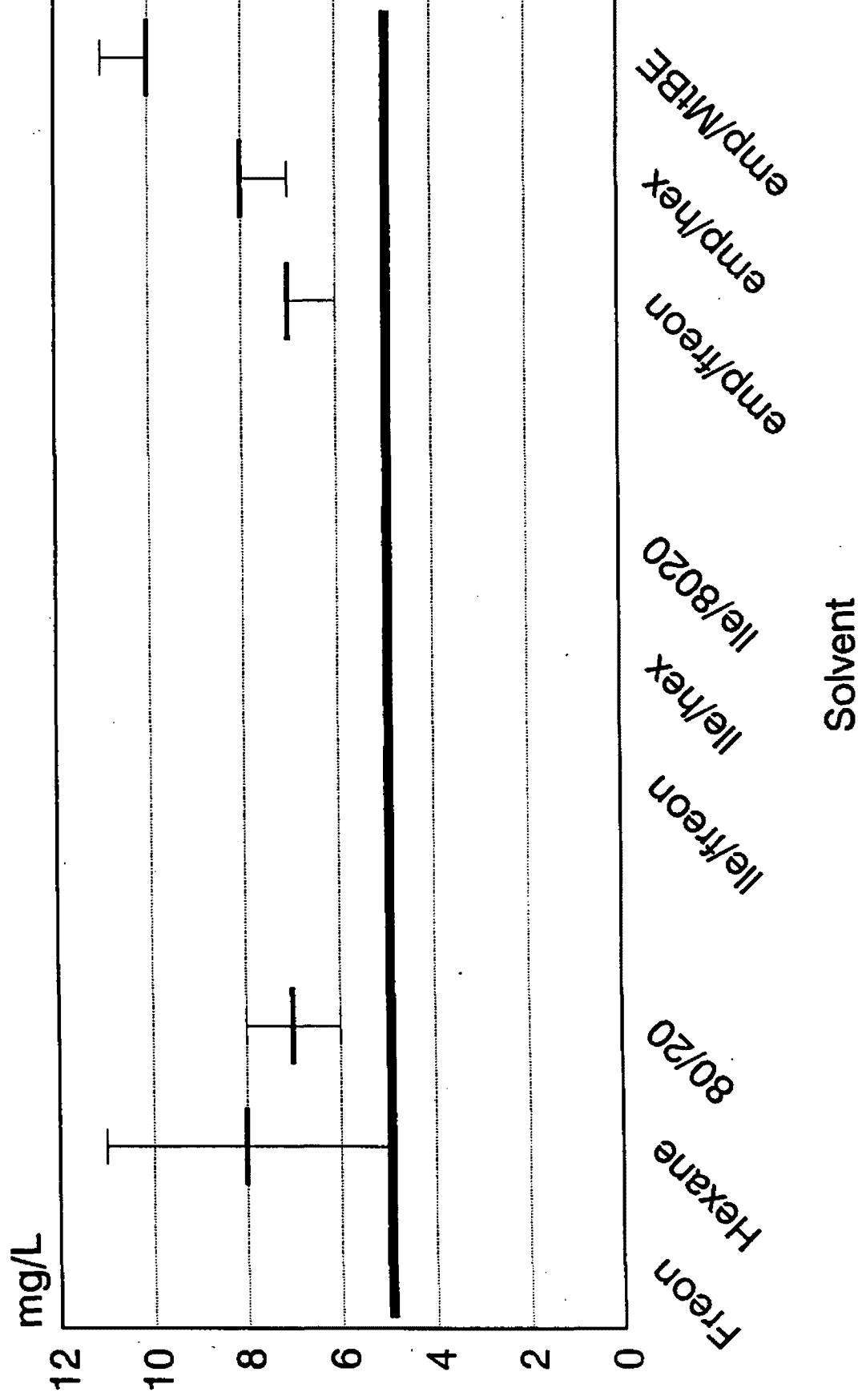
DAF Influent #23457



Flow rate=17 min/L

# Soup Plant

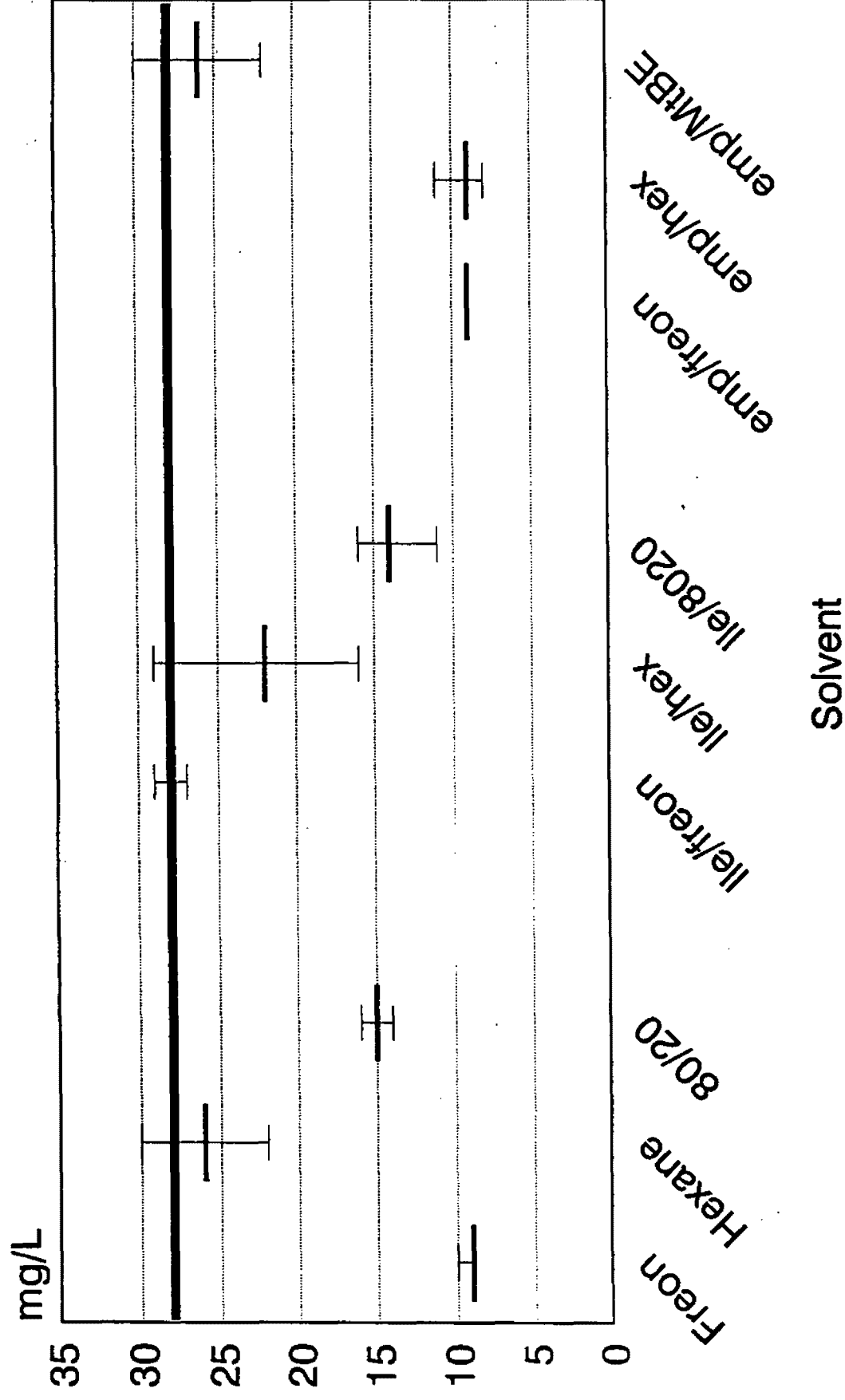
DAF Effluent #23466



Flow rate=44 min/L

# Oily Water Treatment Plant

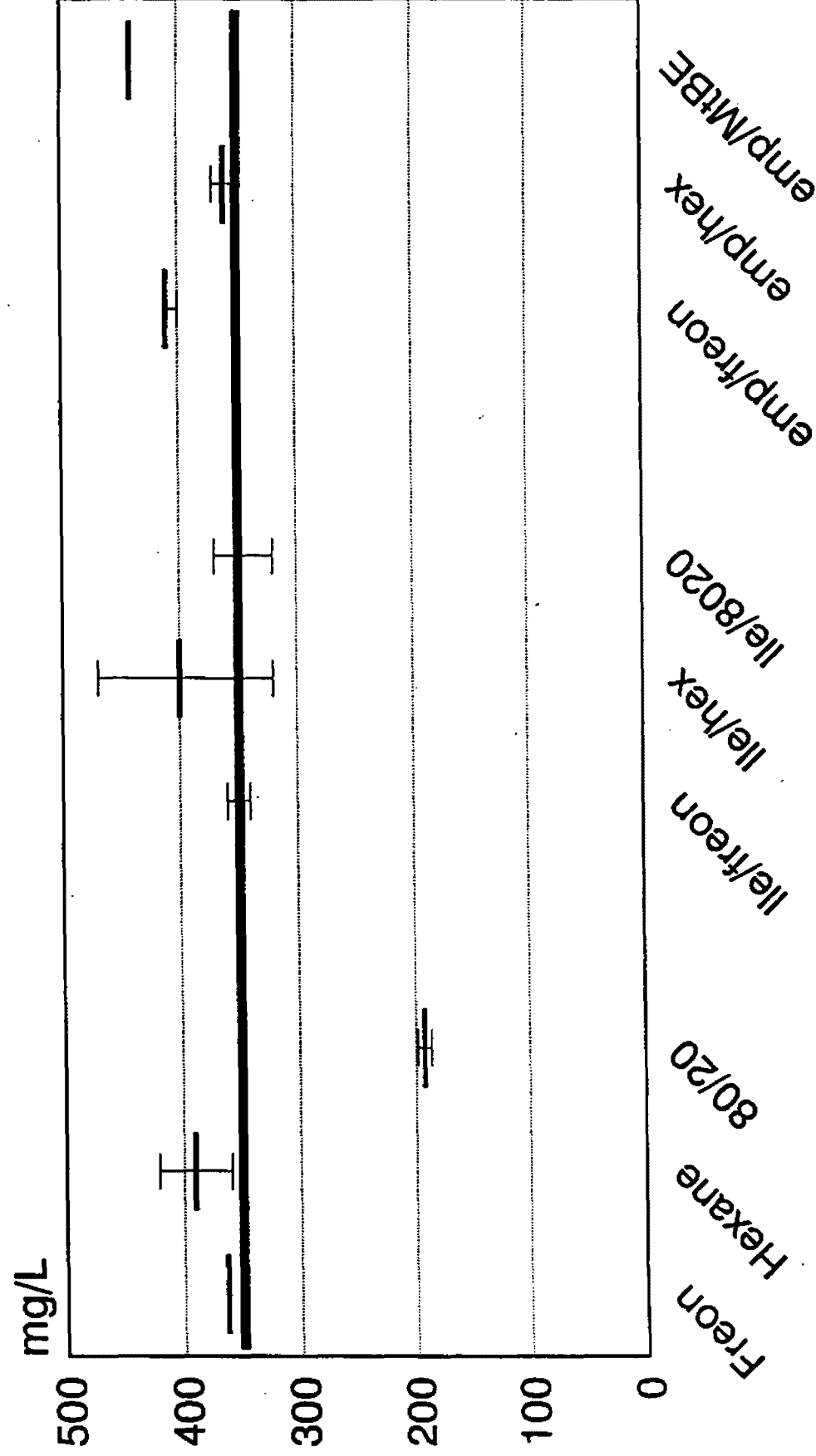
Separator Effluent #23468



Flow rate=18 min/L

# Can Manufacturing Plant

DAF Influent #23470

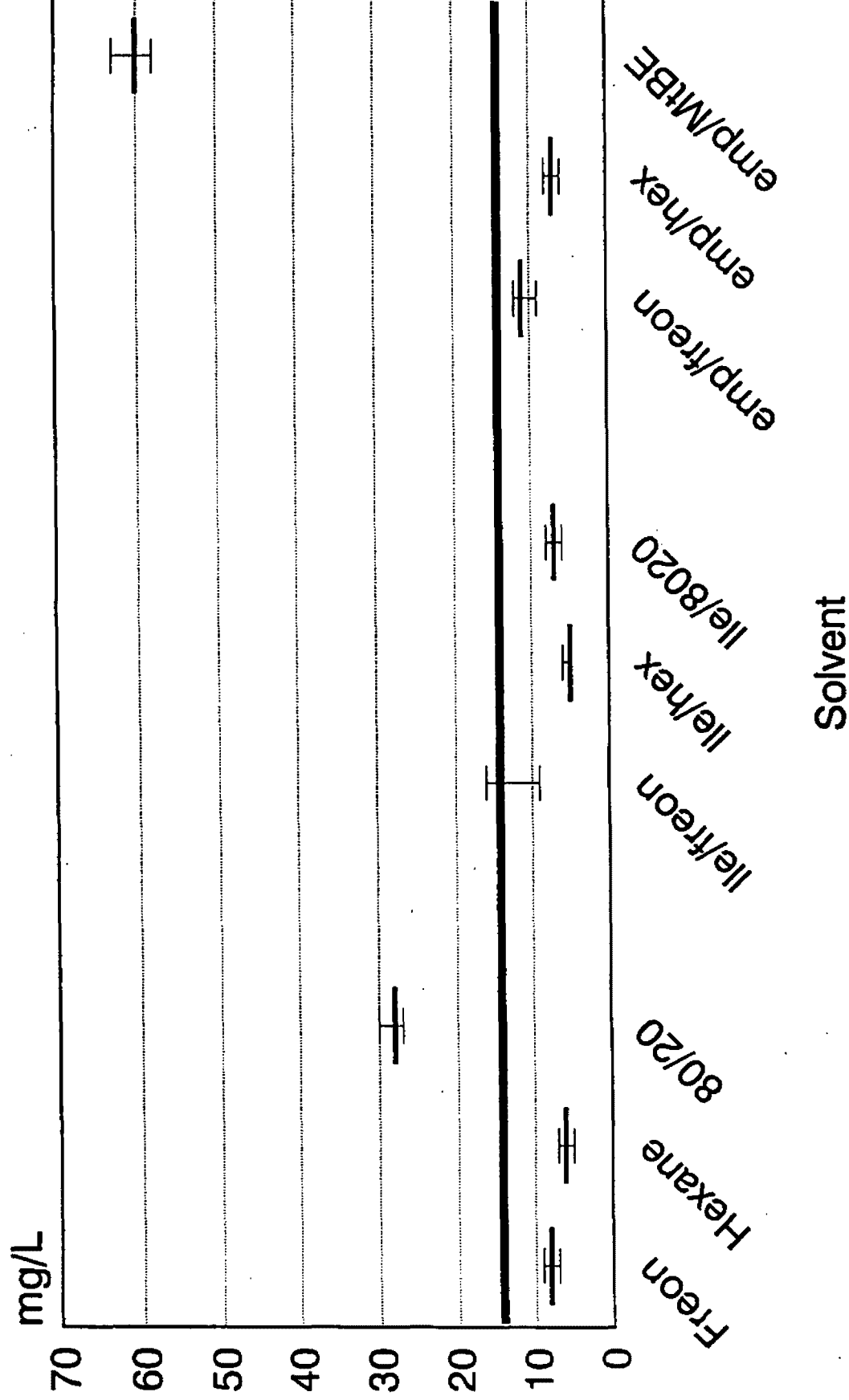


Solvent

Flow rate=14 min/L

# Can Manufacturing Plant

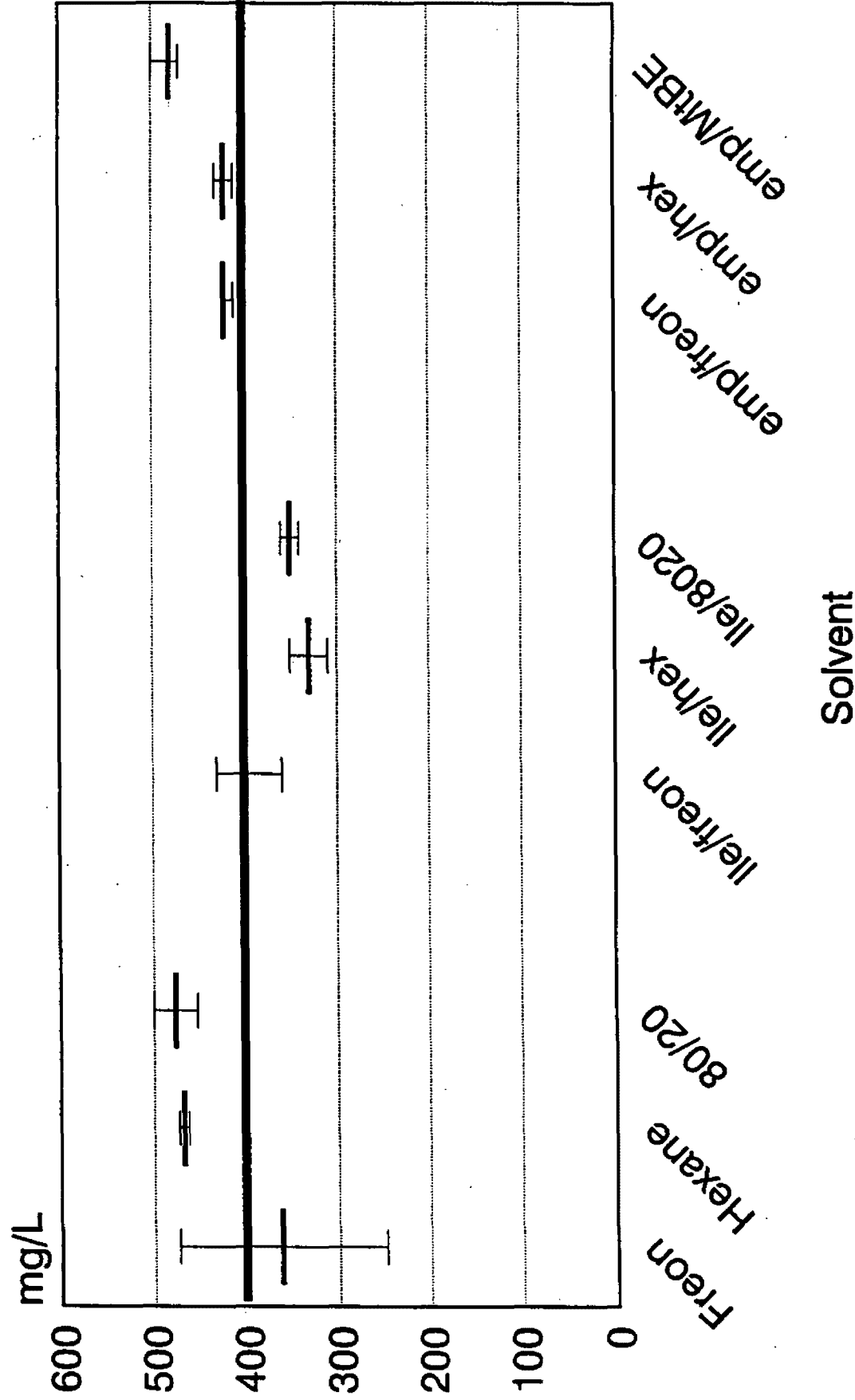
DAF Effluent #23472



Flow rate=14 min/L

# Can Manufacturing Plant

DAF Influent #23473

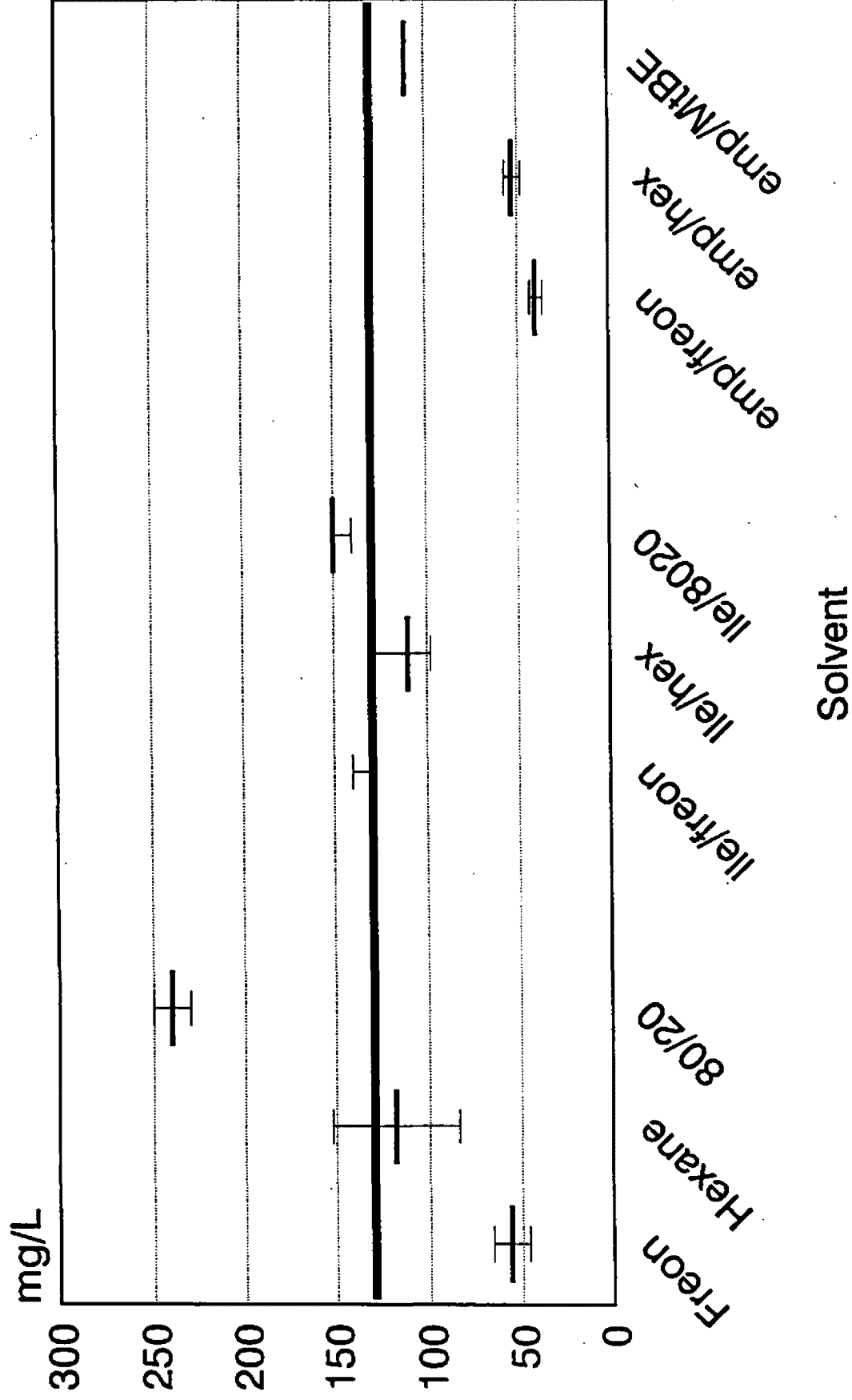


Flow rate = 16 min/L



# Drum Handling Facility

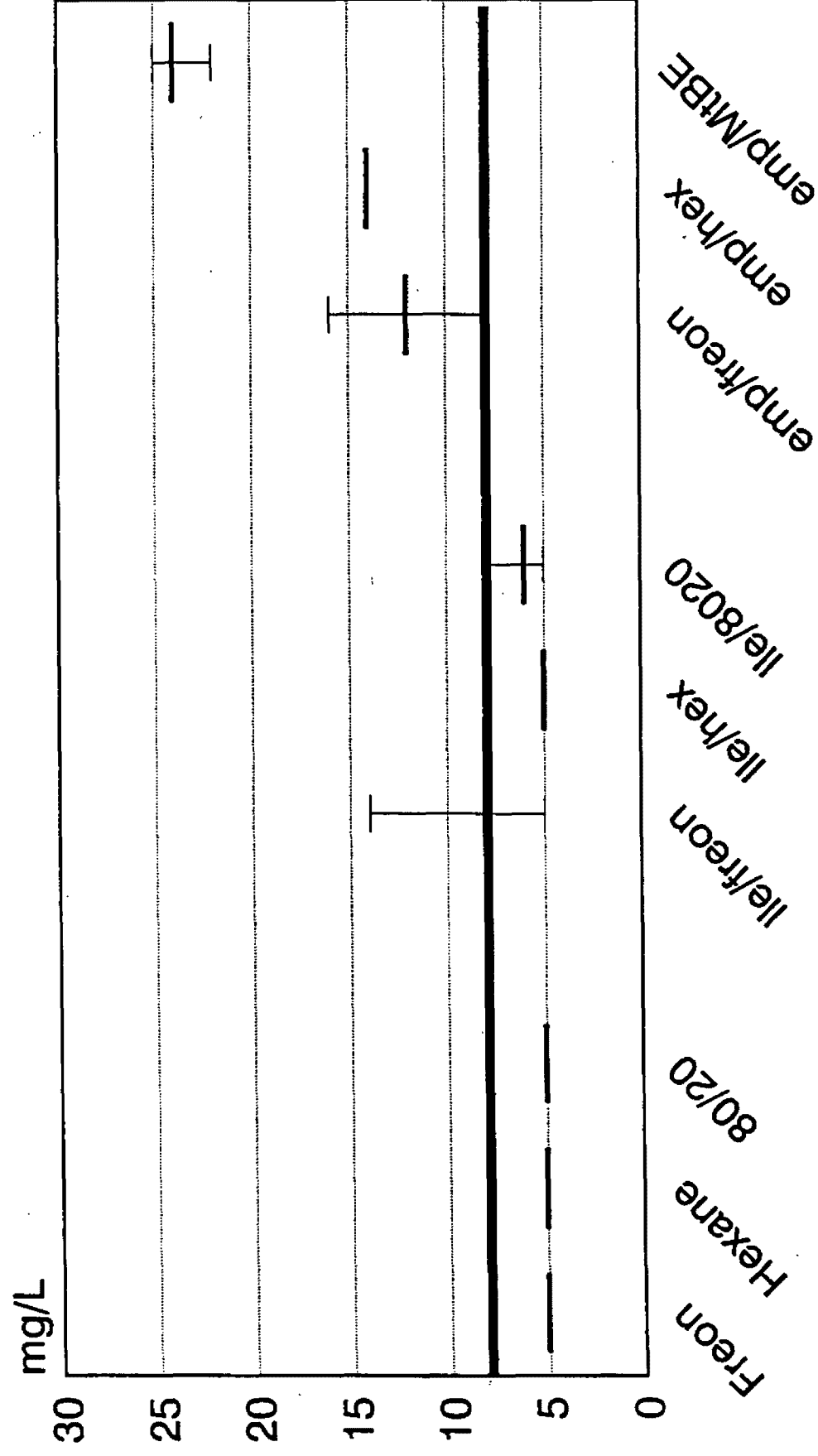
Filter Effluent #23475



Flow rate=20 min/L

# Polymer Plant

Secondary Effluent #23477

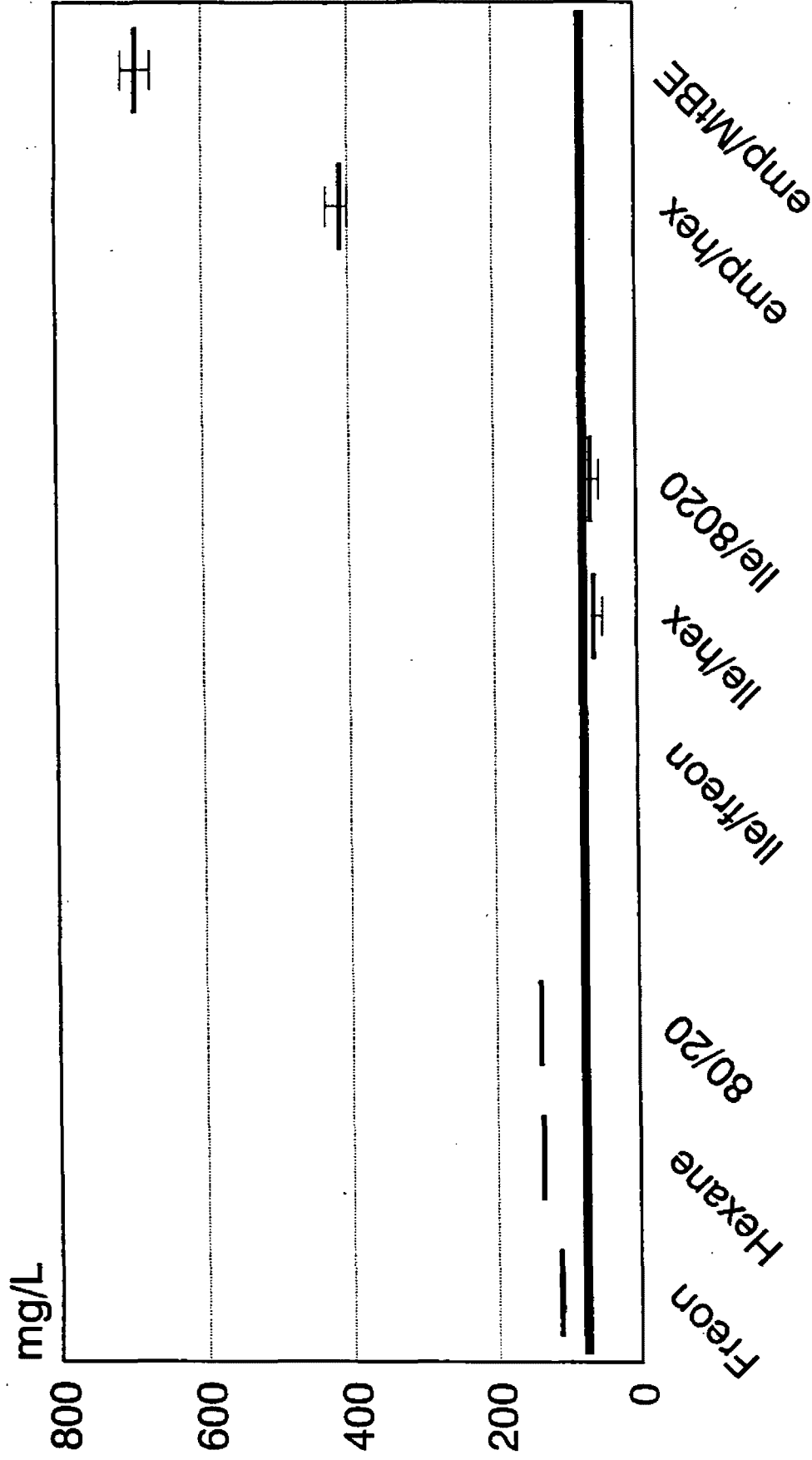


Solvent

Flow rate=26 min/L

# Formulating Plant

Primary Effluent #23481

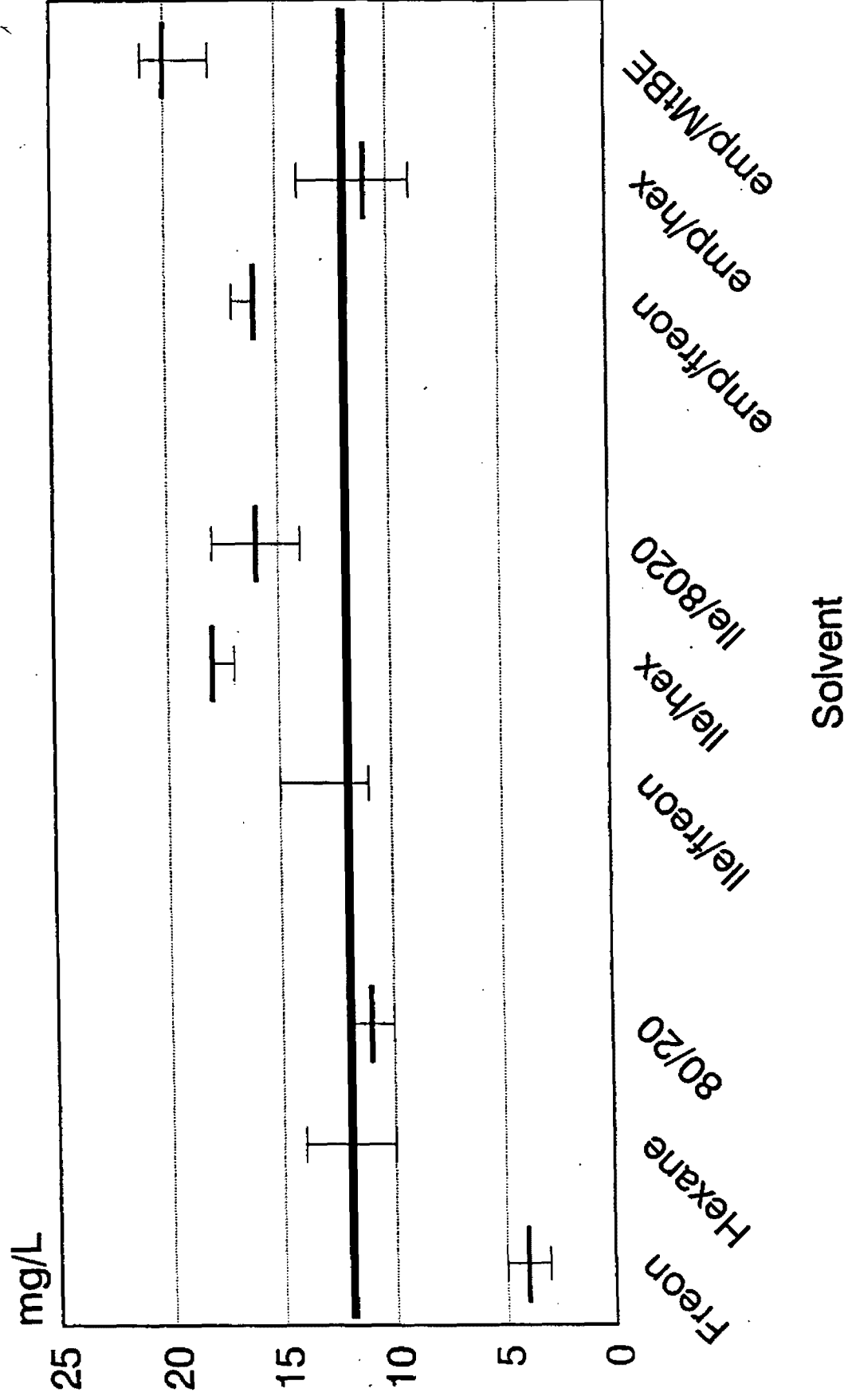


Solvent

Flow rate=153 min/L

# Petroleum Refinery

API Separator Effluent #23484



Flow rate=14 min/L

# Polarity Relationship

"Real World" Samples

	Hexane	Freon	DCM
Average Value	0.91	0.73	2.03
Approximate Polarity Index	0.1	0.01	3.1

Normalized to 80/20

# General Observations and Comments

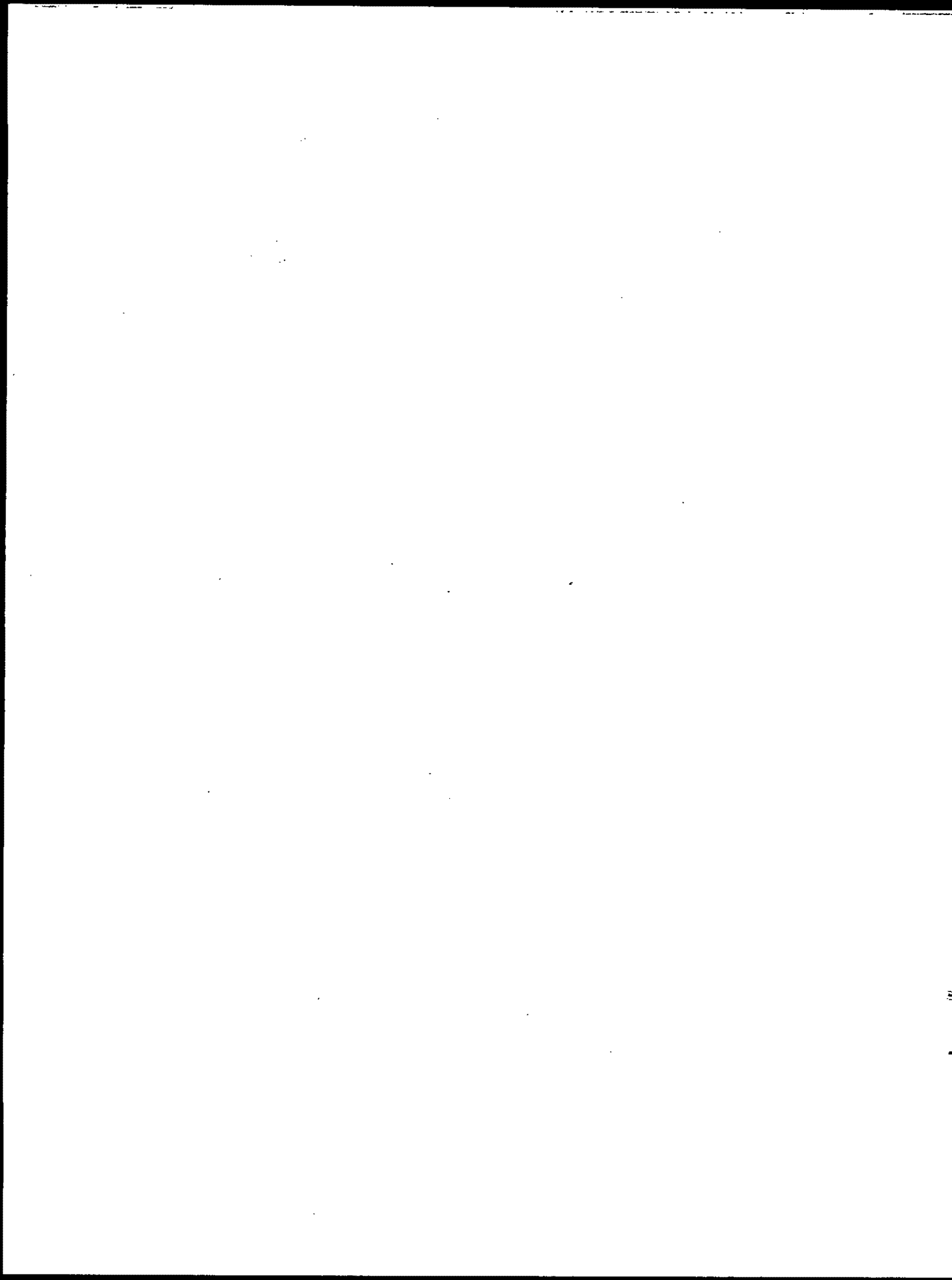
- ◆ Matrix/analyte problems
- ◆ Uniqueness of Freon as an extraction solvent
- ◆ Polarity relationship
- ◆ Difference of extraction and elution solvents

## **Appendix E**

### **Presentation Materials**

#### **"Oil and Grease Analysis in Wastewater Using Solid Phase Extraction Disks"**

**Craig Markell, The 3M Corporation**





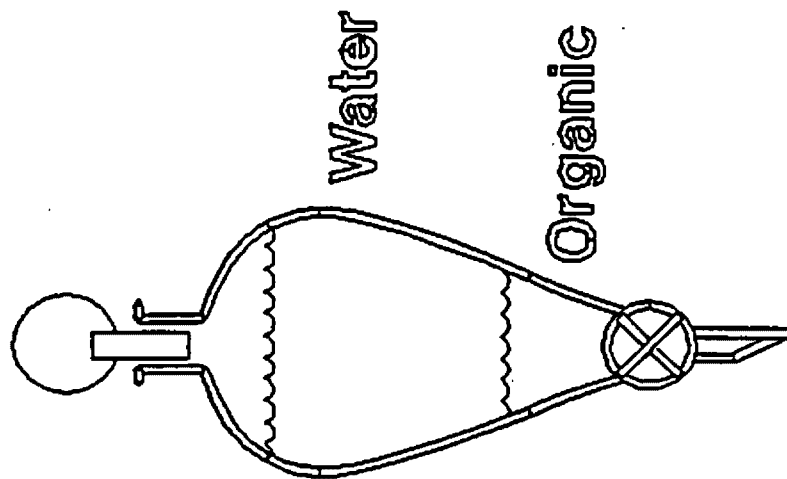
# ***Oil and Grease Analysis in Water Using SPE Disks***

**Craig Markell and Eric Wisted, 3M**

# **General Problem - Extraction of Hydrophobic, Semivolatile Organics from Water or Soil Extracts**

LLE

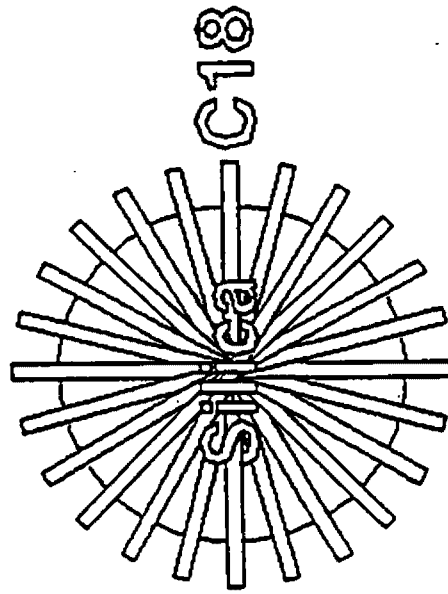
1. Organic Solvent
2. High Surface Area from Shaking



SPE

Organic Solvent = C18 Chains

Surface Area = 500 m<sup>2</sup>/g  
(50 Ft x 50 Ft for 0.5 g)



# ***SPE Disk Method***

1L Sample, pH 2

Condition 90mm C18 Disk + Filter Aid With MeOH

Filter Sample

Elute Disk w. 2 x 15 ml

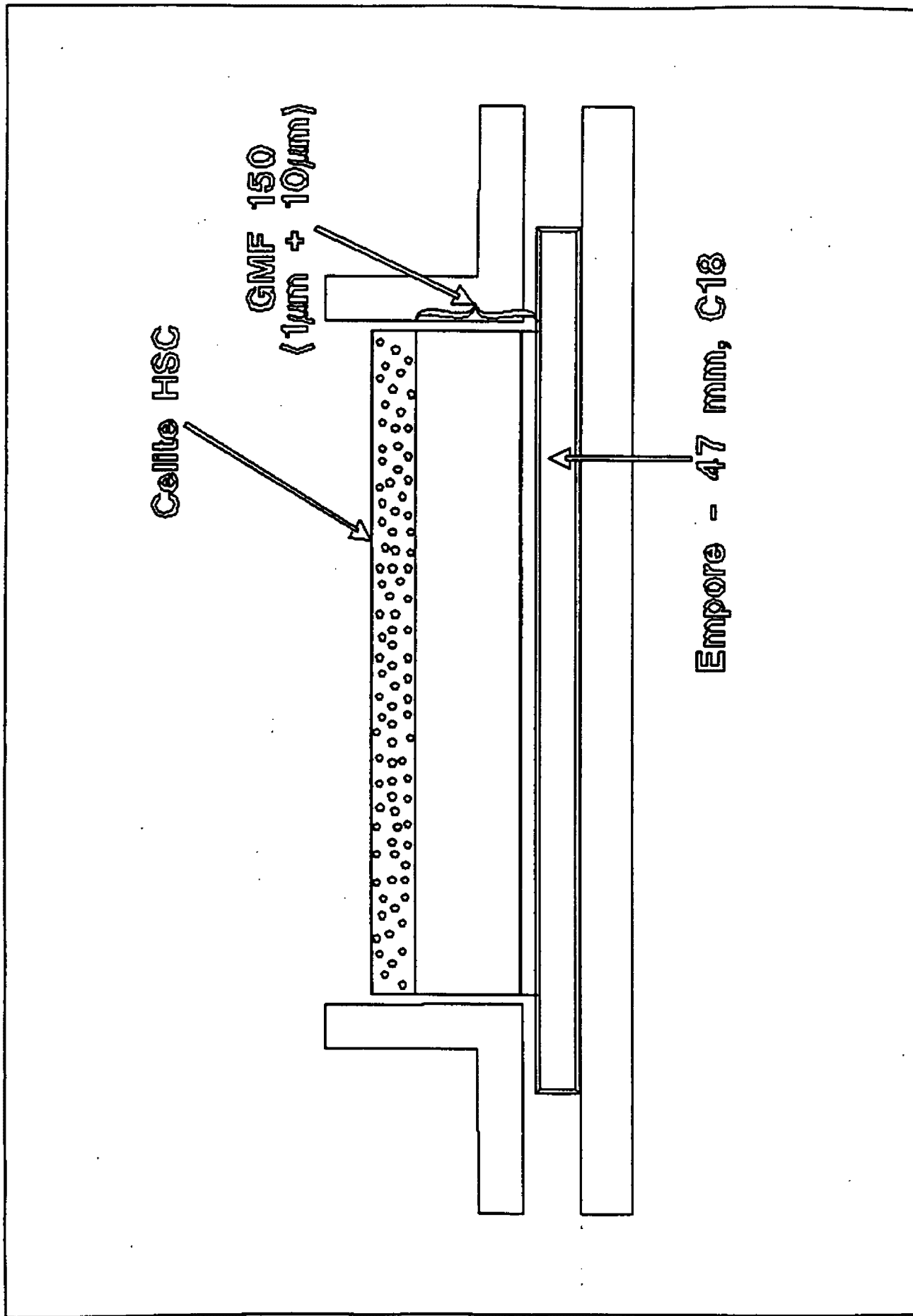
$\text{Na}_2\text{SO}_4$

Concentrate Solvent to <5 ml

Syringe-End Filter Into Tared Vial

Concentrate Remaining Solvent

Weigh Residue



SPC-11

# ***Capacity***

**413.1 = 5-1000 mg/L**

**SPE Capacity?**

**Hydrophobic (Insoluble) Vs. Hydrophilic (Soluble)**

# ***Selectivity***

**Oil and Grease = Any Extractables**

**LLE Results =  $\int$ (Solvent, Solvent Volume, Analyte)**

**SPE Results =  $\int$ (Analyte, Sorbent, Sorbent Mass, Elution Solvent)**

**Freon Results  $\neq$  Replacement Results**

**NPDES Permits?**



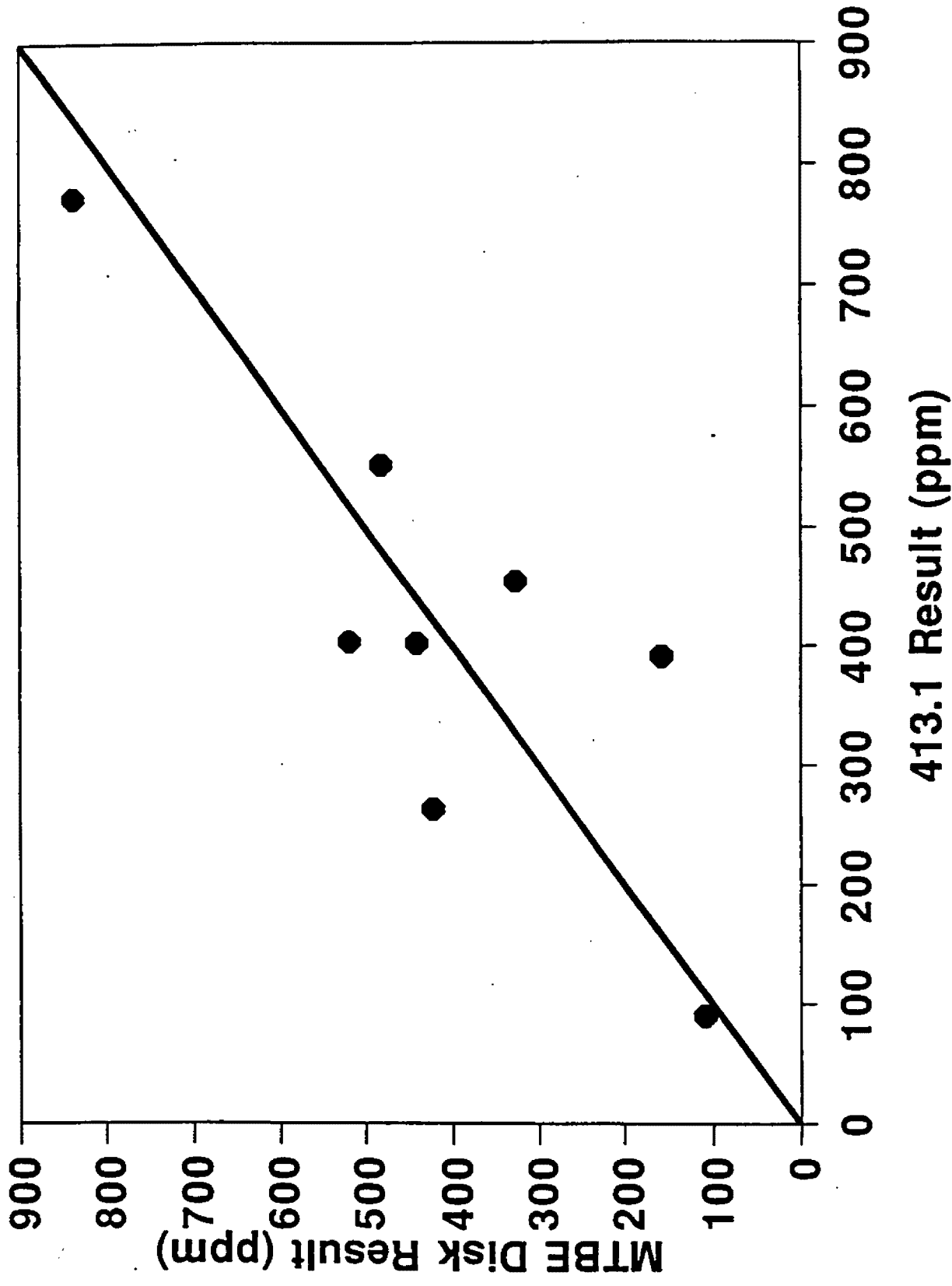
# ***Disk Results Vs. Elution Solvent***

	<u>MTBE</u>	<u>DCM</u>	<u>PERC</u>	<u>FREON</u>	<u>HEXANE</u>
Poultry Plant	837	1717	906	768	738
Railroad Yard	158	88	48	56	66
Soup Plant	10	9	7	7	8

# Results - Disk Vs. 413.1 - High Levels

	<u>Disk</u>		
	<u>MTBE</u>	<u>FREON</u>	<u>413.1</u>
Soap	518	--	403
Meat	837	768	770 C
Transportation	158	56	391 C
Can	422	370	263 C
Laundry	327	255	454 C
Can	440	406	402 OSC
Can	481	426	551 OSC
Drum Recond.	109	40	90 OSC

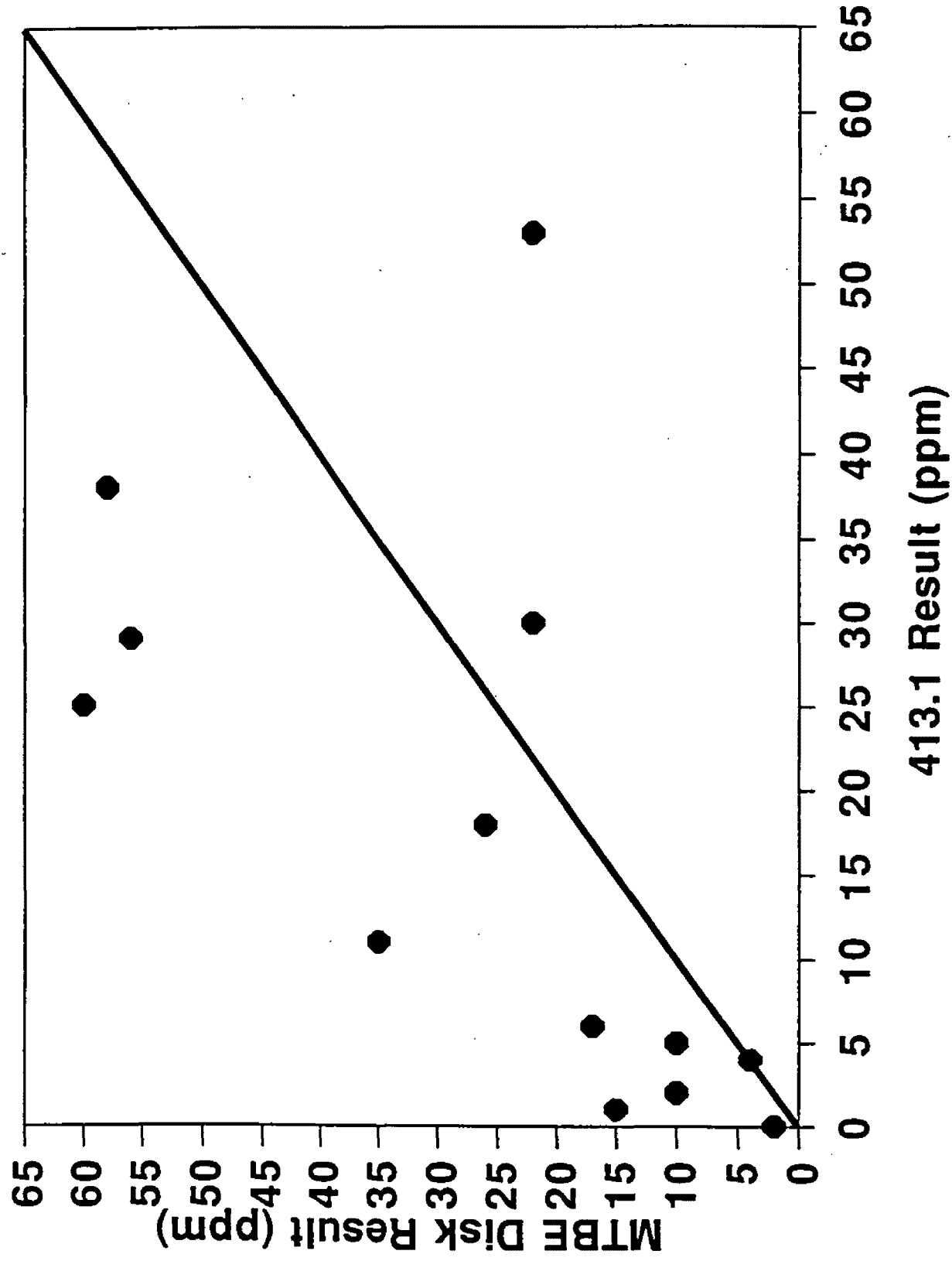
# Results - Disk Vs. 413.1 - High Levels



# Results - Disk Vs. 413.1 - Low Levels

	<u>Disk</u>		
	<u>MTBE</u>	<u>FREON</u>	<u>413.1</u>
Metal	22	--	53
Meat	58	--	38
Metal	2	1	0
Oil	15	1	1
Food	35	1	11
Seafood	10	2	2
Abrasives	4	2	4
Oil	17	3	6 C
Seafood	56	11	29 C
Meat	22	11	30 C
Foods	10	7	5 C
Oil	26	9	18 OSC
Can	60	11	25 OSC

# Results - Disk Vs. 413.1 - Low Levels



***Disk RSD - MTBE, 90 mm***  
***(21 Samples)***

**Average = 6**

**Range = 0-23**

# ***Conclusions***

- **Nothing Will Duplicate 413.1**
- **Disks Work for Oil and Grease**
- **Filtration Times - Most < 1 Hr.**



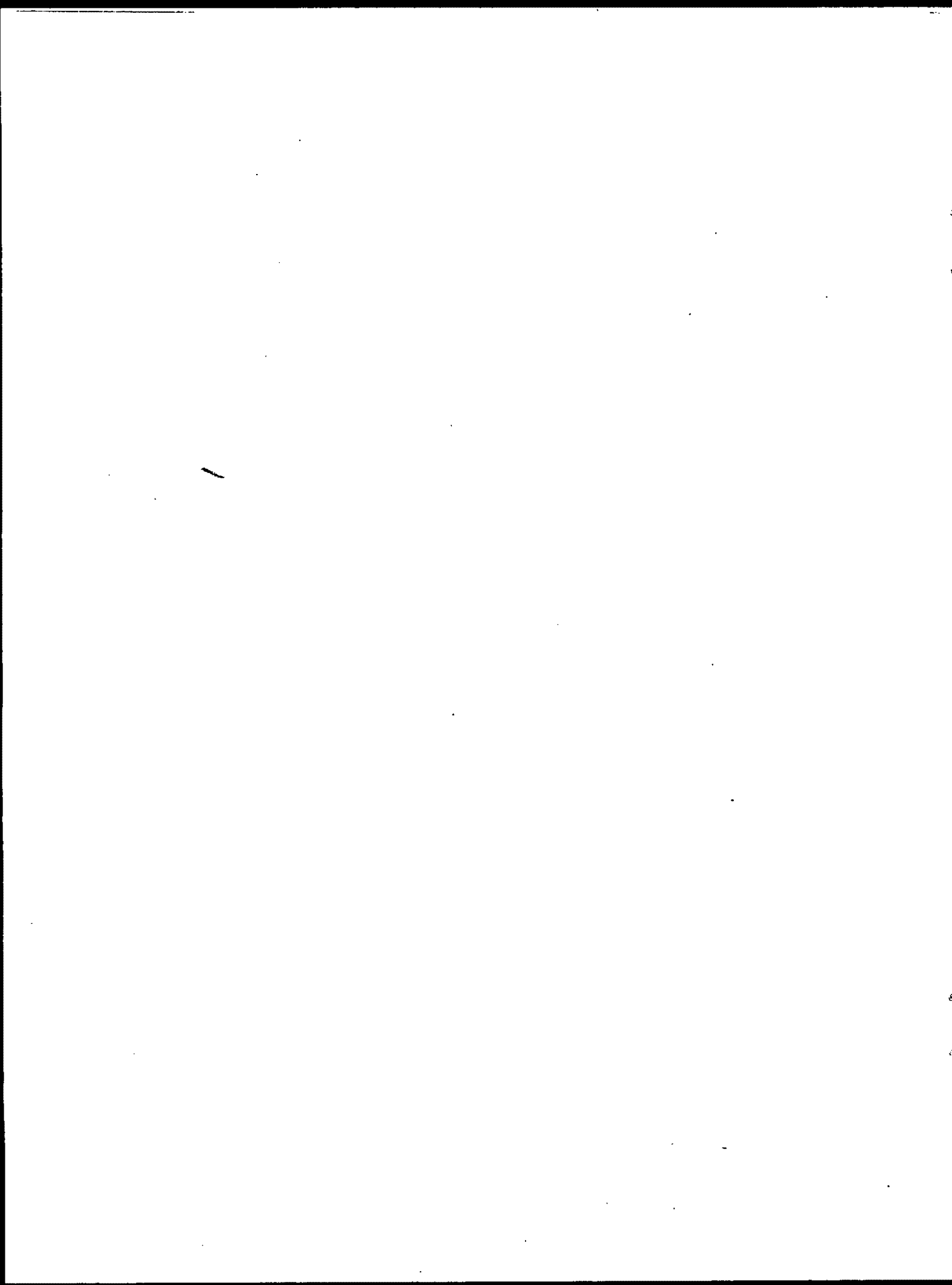


**Appendix F**

**Presentation Materials**

**"Evaluation of Oil and Grease Samples Using NDIR  
and Flon S-316"**

**William Eckel, DynCorp Viar, Inc.**



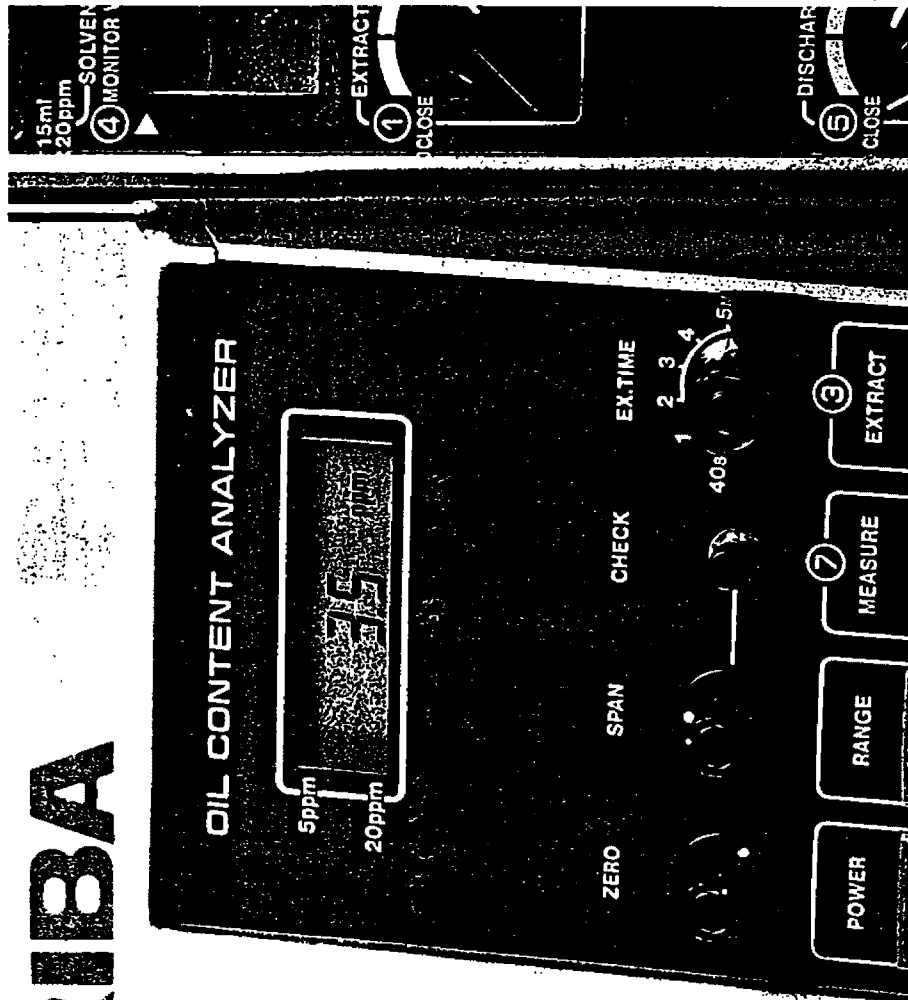
# HORIBA

## OCMA-220 Oil & Grease Analyzer

Slick and Quick Analysis  
For Oil and Grease  
In Soil and Water  
Without Toil and Waste

- EPA 413.2/418.1 type measurement: NDIR detection
- Simple to use: 8 easy steps silkscreened on the panel:
- Compact: perfect for crowded benches and mobile labs

For more information contact:  
HORIBA Instruments Inc.  
17671 Armstrong Avenue  
Irvine, California 92714  
or call: 1-800-4-HORIBA  
In Calif. call: 714-250-4811



**Exhibit 10.**

**Summary Statistics For Alternative Techniques in the Determination of Oil and Grease  
Aqueous Waste Stream, Infrared Analysis**

All Samples (N=36)					
Solvent	Mean	SD	RSD	Median	RMSD
Sep. Funnel Freon	1.00	--	--	1.00	1.5*
Flon	1.62	1.55	96	1.01	8.3
Non-Petroleum (N=13)					
Solvent	Mean	SD	RSD	Median	RMSD
Sep. Funnel Freon	1.00	--	--	1.00	2.0*
Flon	2.33	2.29	98	2.05	9.4
Petroleum (N=23)					
Solvent	Mean	SD	RSD	Median	RMSD
Sep. Funnel Freon	1.00	--	--	1.00	1.7*
Flon	1.21	0.71	58	1.00	6.4

\* Acceptance Limit

\*\* Value Below Acceptance Limit

Mean = Mean of Solvent to Freon Ratios

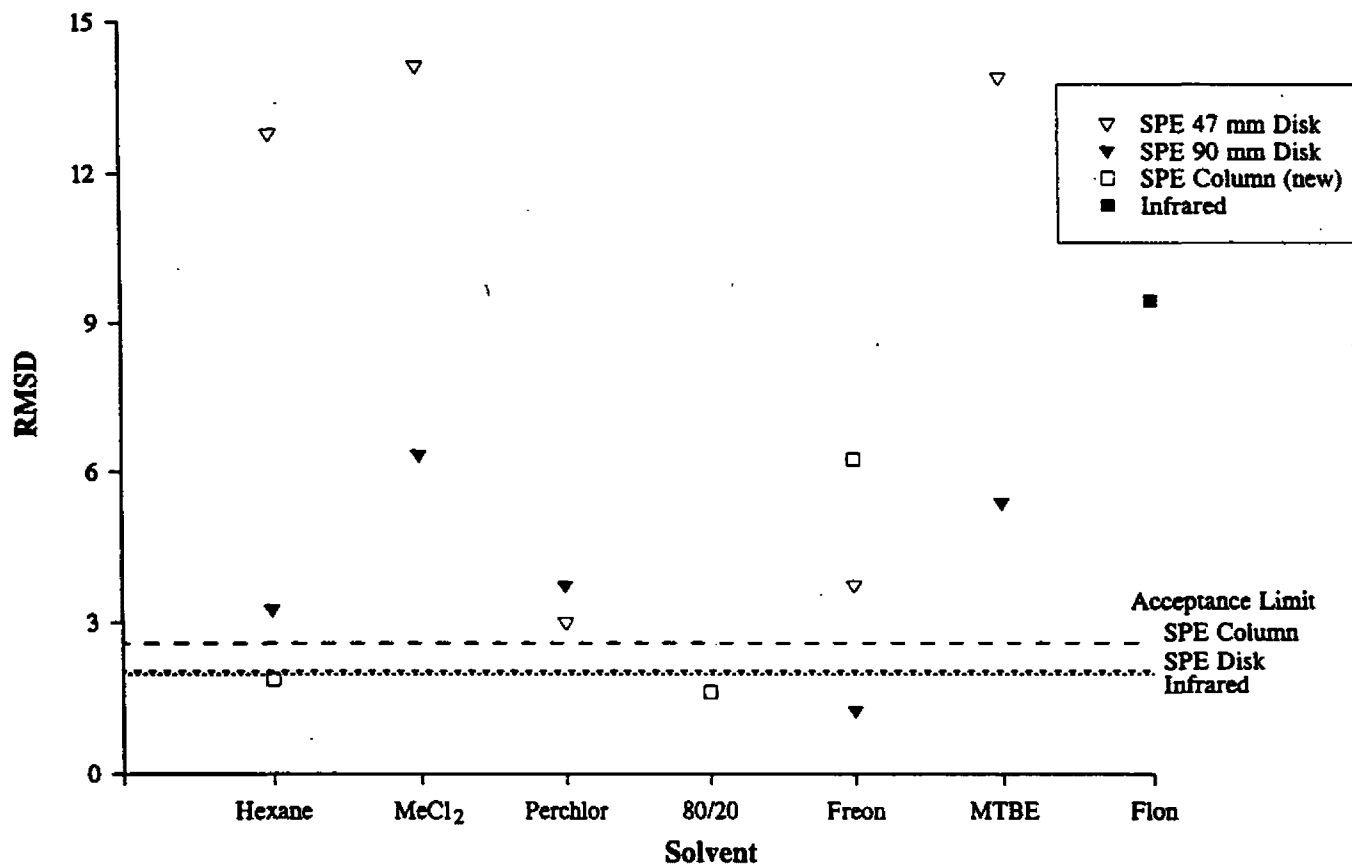
SD = Standard Deviations of Solvent to Freon Ratios

RSD =  $100 \times \text{SD}/\text{Mean}$

Median = Median of Solvent to Freon Ratios

RMSD = Normalized Root Mean Square Deviation of Sample x Solvent Means

Exhibit 14.  
Normalized Root Mean Square Deviations  
Aqueous Waste Stream, Alternative Techniques  
Non-Petroleum Samples



NOTE: Points below the respective Acceptance Limit are not significantly different from separatory funnel extraction with Freon

Exhibit 15.  
Normalized Root Mean Square Deviations  
Aqueous Waste Stream, Alternative Techniques  
Petroleum Samples

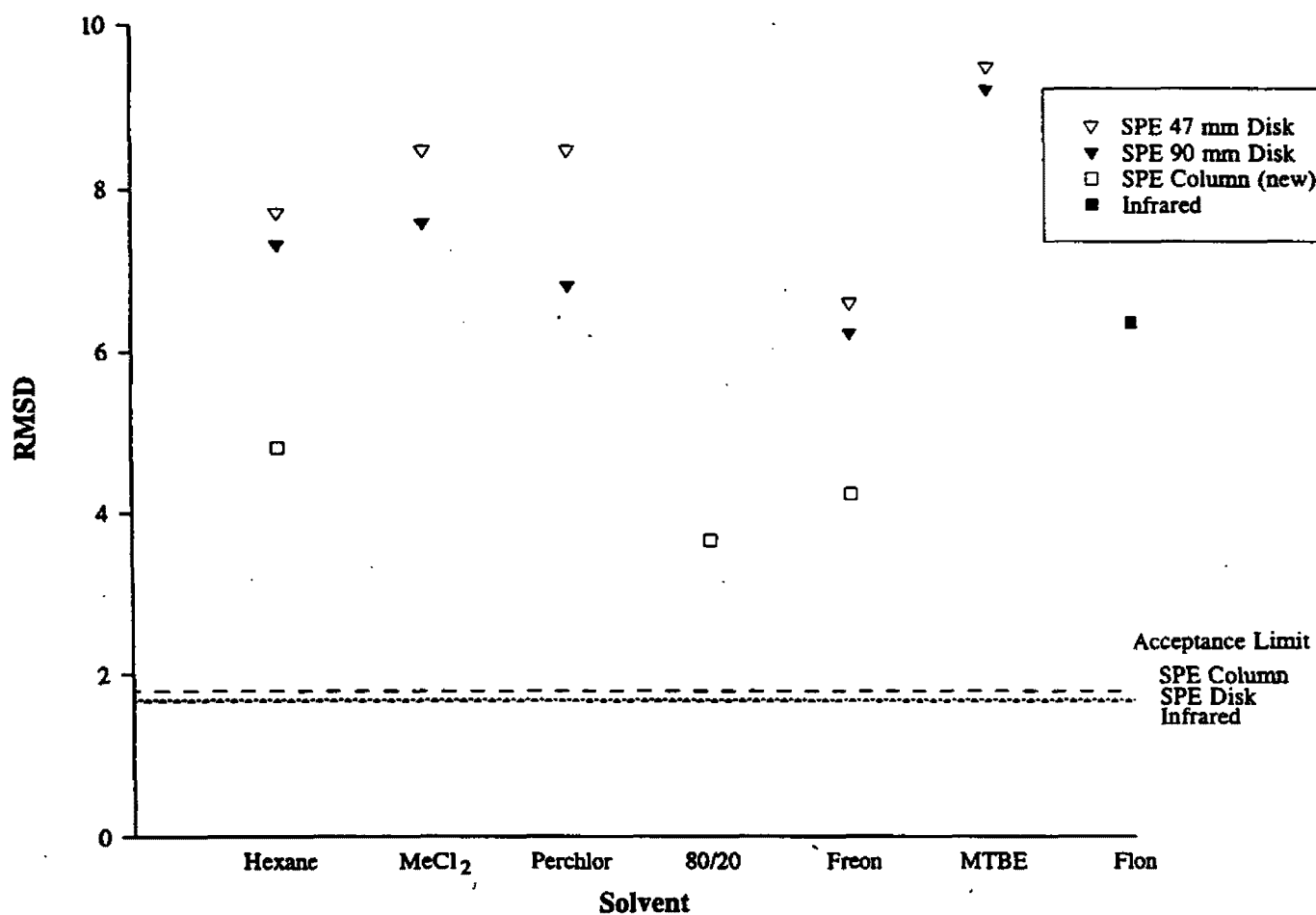
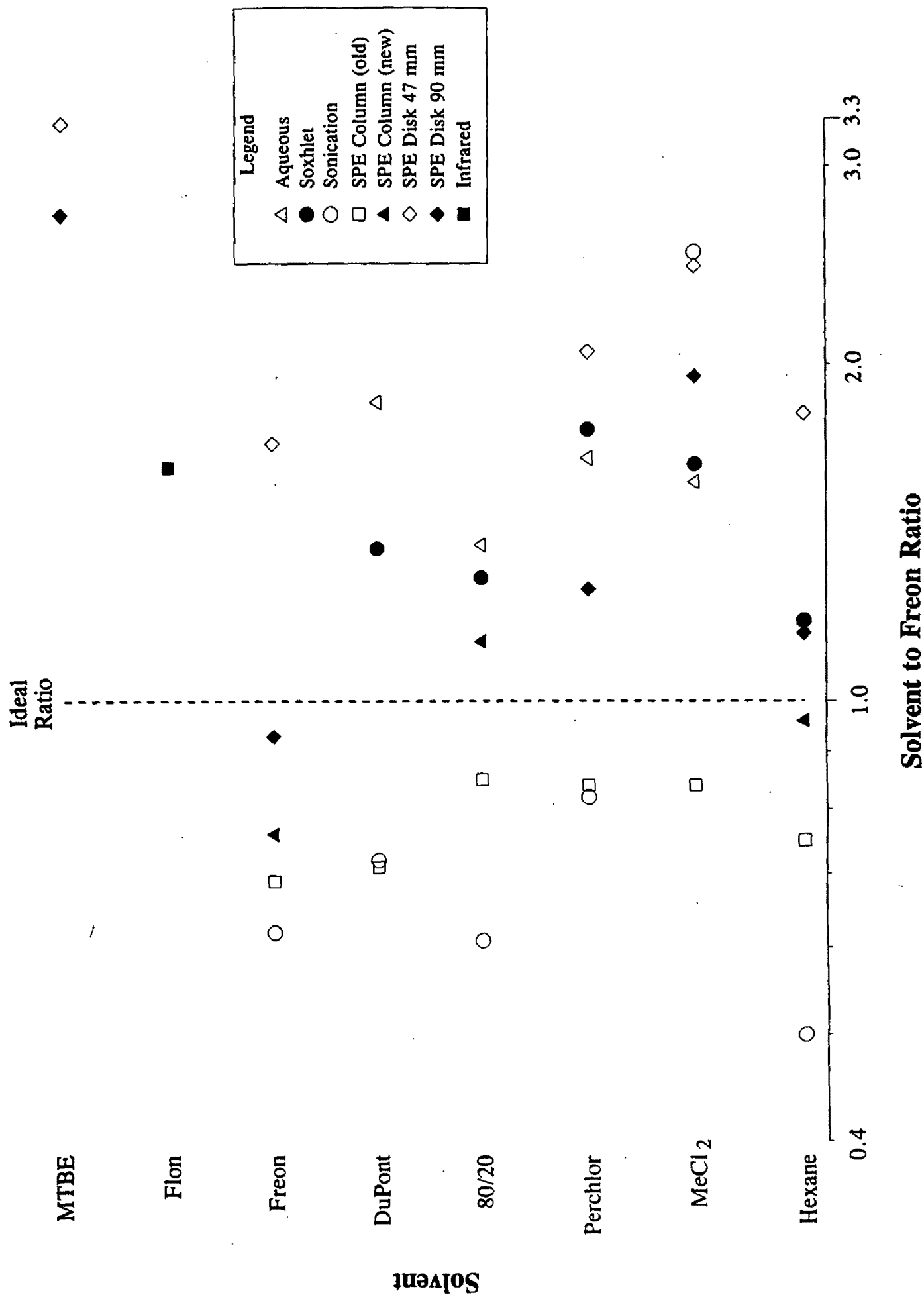
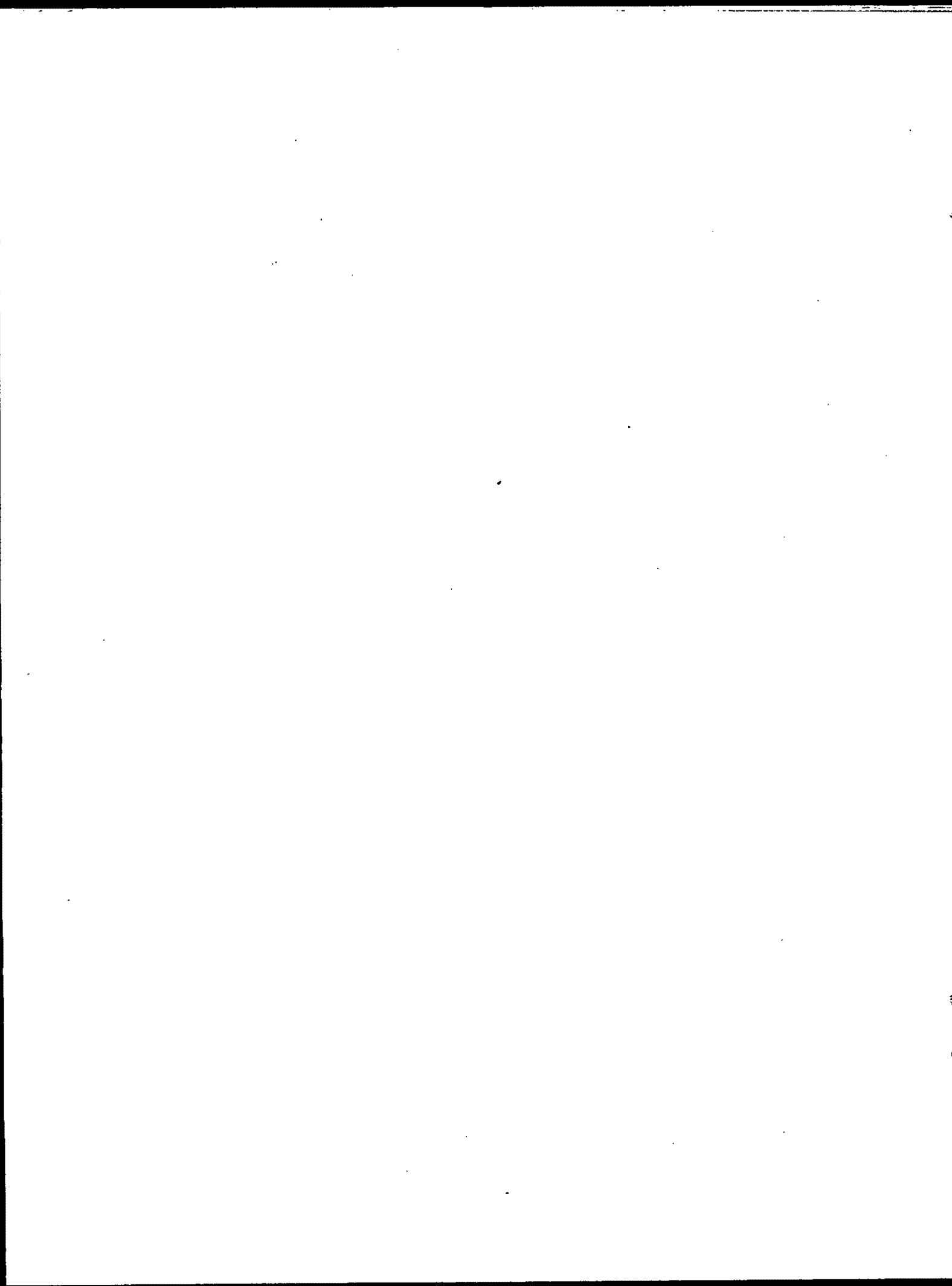


Figure 7

# Mean Solvent to Freon Ratios For All Techniques Tested





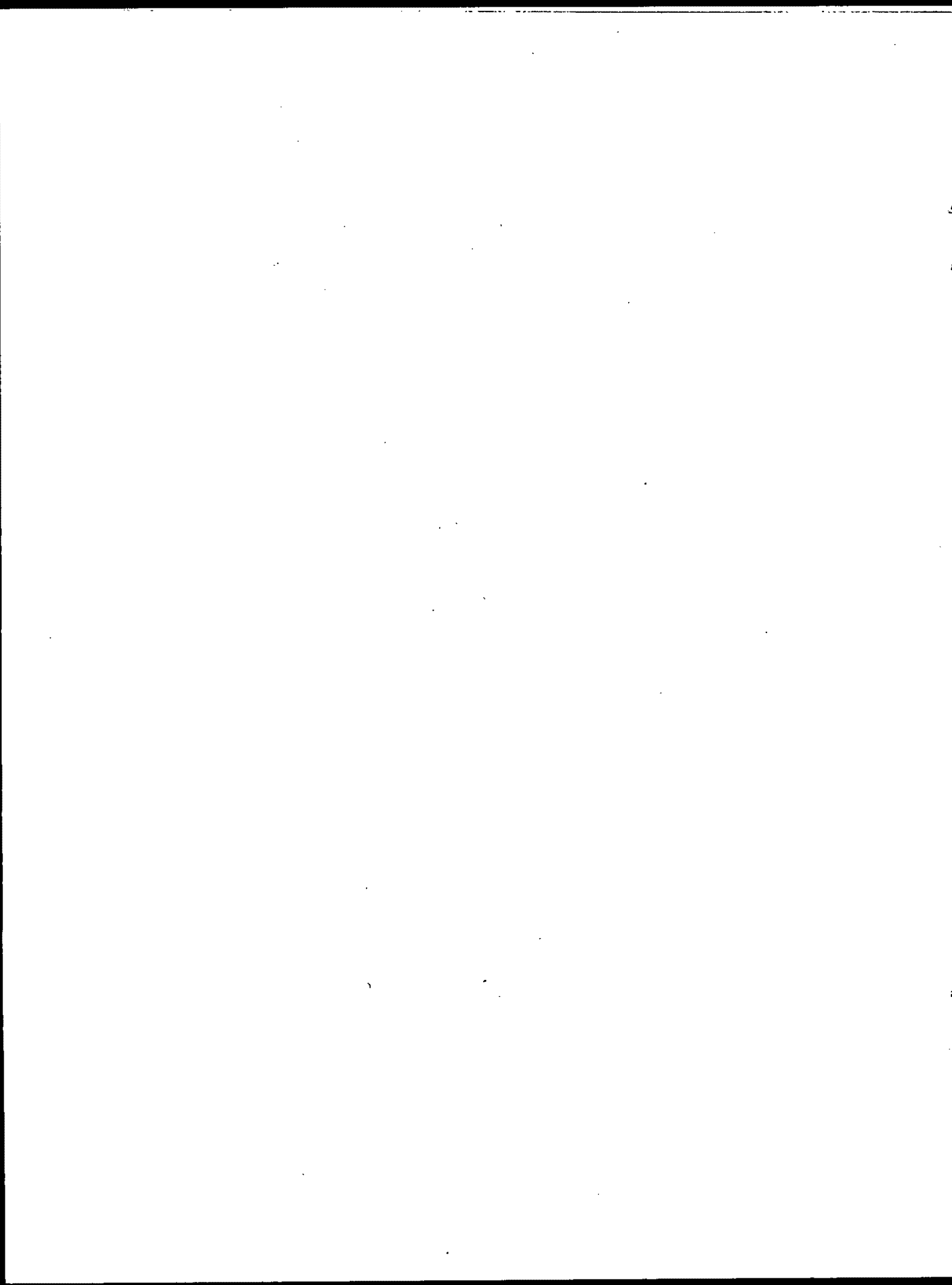


## **Appendix G**

### **Presentation Materials**

**"Determination of Oil and Grease by Evaporation of Solvent  
in a Quartz Cell in an Infra-red Spectrophotometer"**

**Gerald DeMenna, Chem-Chek Laboratories**





**BUCK Scientific, Inc.**

58 Fort Point Street • East Norwalk, Connecticut 06855 • (203) 853-9444

Ms. Lynn Riddick  
EPA

Material from Oil & Grease lecture in Norfolk, VA

**ENVIRONMENTAL OIL & GREASE  
ANALYSIS: An Overview**

A NOVEL Technique for using LESS Freon  
and non-"Freon" solvents  
[Using existing IR Photometers]

Gerald J. DeMenna, Chem-Chek Consulting  
44 Stelton Road, Piscataway, NJ 08854  
[908] 752-7793

16th. Annual EPA Meeting // 4 May 1993  
Norfolk, Virginia

**CURRENT METHODOLOGIES:**

- [1] Extraction and Gravimetric Isolation  
of TPH materials
- [2] Extraction and Liquid Cell IR Filter  
Photometry of TPH (C-H) Absorptions
- [3] Gas Chromatographic Separation  
with FID Detection for TPH

**PROPOSED PROCEDURE:**

For use with existing Infra-Red filter Photometers  
optimized for the 3.4 micron / 2950 cm<sup>-1</sup> absorption  
bands found in ALL hydrocarbon materials  
without using large volumes of FREON or  
using non-FREON type solvents (Methylene Chloride)

**PROPOSED PROCEDURE:**

- [1] Prepare the sample and perform the extraction per standard protocols (SW-846 / #9070-9071)
- [2] Downscale the Volume or Weight of FREON used for the extraction by a factor of 2 to 10 [dependant on sample matrix]
- [3] "Cast" a film of TPH material from the FREON on a IR-Quartz "cavity" cell

**INSTRUMENTATION:**

Model HC-404 Total Petroleum Hydrocarbon analyzer

[Filter IR Photometer w/ 20 cm-1 bandpass at 3.42 microns]

Normal Analyses w/ 10mm. IR-Quartz Liquid Cell using Freon-113

Purchased from BUCK Scientific, Inc.,  
E. Norwalk, CT

**PRINCIPLES:**

Like the existing gravimetric procedure, the "evaporation method" will allow the Freon solvent to volatilize and leave the TPH materials as a film residue in a IR-transparent Quartz plate.

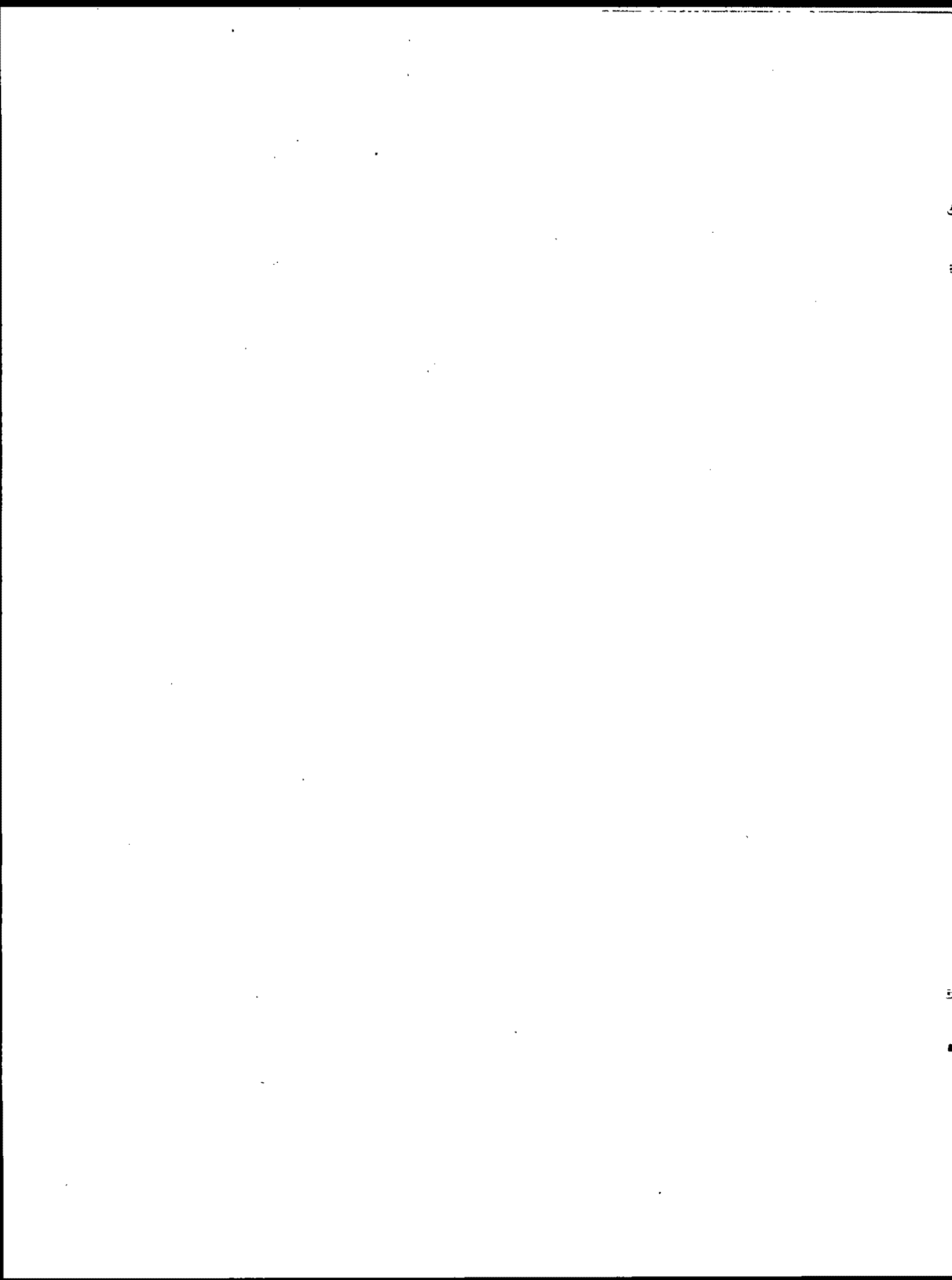
Standards and spikes carried through the procedure are used for calibration and recovery calculations.

## **Appendix H**

### **Presentation Materials**

#### **"Phase I Study Conclusions and Strategy Options for Regulation Oil and Grease"**

**William A. Telliard, U.S. EPA Office of Water**



# **PHASE 1 CONCLUSIONS**

---

- Retain *n*-hexane
  - Results for petroleum-based solids & non-petroleum aqueous samples are below Acceptance Limit
  - Was used in oil and grease measurements before Freon 113
- Retain perchloroethylene
  - Results for non-petroleum aqueous samples are below Acceptance Limit
  - Can be used in the measurement of oil and grease by infra-red techniques.

## **PHASE 1 CONCLUSIONS**

- Retain *n*-hexane/MTBE (80/20)
  - Results produced are below the Acceptance Limit for petroleum-based solids
  - The solvent developed by EMSL-Ci in the preliminary study
- Eliminate methylene chloride
  - Results produced using this solvent are not below Acceptance Limit for any category of samples



## **PHASE 1 CONCLUSIONS**

- **Eliminate DuPont 123**
  - Results produced using this solvent are not below Acceptance Limit for any category
  - DuPont 123 is a Class II CFC that will need to be phased out eventually
- **Alternative techniques**
  - Only sonication of non-petroleum solids produced results equivalent to existing techniques with Freon 113.
  - Smaller solvent volumes required by SPE and increased sensitivity of NDIR might warrant further study

# OPTION

---

- Stop monitoring oil and grease

5/3/93

52-001-14A

# OPTION

---

- Select one solvent/extraction technique that produces the closest result to Freon across all categories of discharges

# OPTION

---

- Use alternative techniques without Freon as a solvent (e.g., GC, IR)

# OPTION

---

- Obtain a waiver to allow continued use of Freon

5/3/93

52-001-14A

# OPTION

---

- Develop a correction factor

5/3/93

52-001-14A

# OPTION

---

- Turn the entire responsibility over to Environment Canada

5/3/93

52-001-14A





**BENEFITS of NEW PROCEDURE:**

- [1] Allows use of significantly lower volumes of regulated solvents.
- [2] Allows use of other suitable solvents with similar partitioning coefficients  
[methylene chloride for this study]

**Evaluation of Method Correlation:**

Test three (3) varied types of samples for TPH by:

- [1] Gravimetric Technique
- [2] IR Photometer w/10mm. Liquid Cell
- [3] IR Photometer w/ "cavity cell"

\* NOTE - All extractions done with Freon-113

**Sample #1: Polymer Fabrication Plant,  
Elizabeth, NJ / discharge line**

Data from triplicate preps w/ statistics,  
with 5 PPM spike for recovery study

[1] GRAV	[2] IR-LIQ	[3] IR-EVAP
-----	-----	-----
25 PPM	31 PPM	28 PPM
(5.5% RSD)	(3.7% RSD)	(4.2% RSD)
31 PPM	36 PPM	33 PPM
[spike recovery 99+% overall]		

**Sample #2: Pharmaceutical Manufacturer,  
Wilmington, DE / pond sludge**

**Data from triplicate preps w/ statistics,  
with 50 PPM spike for recovery study**

<b>[1] GRAV</b> -----	<b>[2] IR-LIQ</b> -----	<b>[3] IR-EVAP</b> -----
140 PPM (3.9% RSD)	155 PPM (2.4% RSD)	150 PPM (3.2% RSD)
195 PPM	202 PPM	201 PPM
[spike recovery 97+% overall]		

**Sample #3: Commercial Development Site,  
Westchester, NY / mixed soil corings**

**Data from triplicate preps w/ statistics,  
with 10 PPM spike for recovery study**

<b>[1] GRAV</b> -----	<b>[2] IR-LIQ</b> -----	<b>[3] IR-EVAP</b> -----
52 PPM (4.1% RSD)	55 PPM (3.4% RSD)	53 PPM (3.0% RSD)
61 PPM	65 PPM	64 PPM
[spike recovery 98+% overall]		

**PRELIMINARY COMPARATIVE STUDY:**

**Freon-113 vs. Methylene Chloride  
on the "cavity cell"**

**Sample: Machinery Shop effluent**

<b>Freon-113</b> -----	<b>CH2Cl2</b> -----
87 PPM (3.3% RSD)	91 PPM (3.5% RSD)

**Performance Specifications**

[based on 250uL aliquot in 5mm x 4mm  
cavity in IR-Quartz plate]

**Sensitivity:** 1.5 PPM gives 0.004A signal

**Detection Limit:** 4 PPM gives 10% reproducibility  
at approx. 0.01A

**Linearity:** Correlation of 0.98 up to 250 PPM

**CONCLUSIONS:**

This technique is adaptable to all  
IR Photometric units with an open sample  
compartment to allow use of the "cavity cell"  
evaporation plate.

Additional studies with other solvents  
and a variety of sample matrices  
is required to fully develop the  
potential usefulness of the method.

