

USE OF MASS SPECTROMETRIC METHODS FOR FIELD  
SCREENING OF VOC'S

J. C. Evans

November 1994

Presented at the  
Air and Waste Management Association Annual Convention  
November 16-18, 1994  
Eugene, Oregon

Prepared for  
the U.S. Department of Energy  
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory  
Richland, Washington 99352

**DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

**MASTER**

## **DISCLAIMER**

**Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.**

# Use of Mass Spectrometric Methods for Field Screening of VOC's

John C. Evans

Earth and Environmental Sciences Center

Pacific Northwest Laboratory

P.O. Box 999

Richland, WA 99352

## ABSTRACT

While mass spectrometric (MS) methods of chemical analysis, particularly gas chromatography-mass spectrometry (GC/MS), have been the mainstay of environmental organic analytical techniques in the laboratory through the use of EPA and other standard methods, field implementation is relatively rare. Instrumentation and methods now exist for utilizing MS and GC/MS techniques in the field for analysis of VOC's in gas phase, aqueous, and soil media. Examples of field investigations utilizing HP 5971A and Viking SpectraTrak systems for analysis of VOC's in all three media will be presented. Mass spectral methods were found to offer significant advantages in terms of speed of analysis and reliability of compound identification over field gas chromatography (GC) methods while preserving adequate levels of detection sensitivity. The soil method in particular provides a method for rapid in-field analysis of methanol preserved samples thus minimizing the problem of volatiles loss which typically occurs with routine use of the EPA methods and remote analysis. The high cost of MS instrumentation remains a major obstacle to more widespread use.

# **Use of Mass Spectrometric Methods for Field Screening of VOC's**

**John C Evans**

**Earth and Environmental Sciences Center  
Pacific Northwest Laboratory**

**Operated for the U.S. Department of Energy  
by Battelle Memorial Institute**

# Statement of Problem

- VOC compounds associated with solvent and fuel releases are a major source of environmental contamination
- Use of standard laboratory methods for all samples can be prohibitively expensive with very long analytical testing and reporting backlogs
- Standard methods are tailored to water samples
- EPA method for soil analysis has large potential for generation of false negatives
- Gases (i.e. soil gas) must be measured promptly with ad hoc methods

# Why MS Methods?

- **GC/MS is widely accepted as the method of choice for laboratory VOC analysis**
- **MS detection provides in general the highest reliability of compound identification**
- **MS detection minimizes requirement for high quality chromatographic separation**
- **Stand-alone MS can provide very rapid analysis of simple combinations of analytes**
- **Modern MS instrumentation is now rugged enough for field deployment**
- **High cost of instrumentation remains a major impediment to widespread field use**

# **Available PNL MS Instrumentation**

- **Direct sampling ion trap MS (ORNL prototype)**
- **Hewlett-Packard HP5971A quadrupole GC/MS with Environmental Devices dimethyl silicone membrane inlet for direct MS operation**
- **Viking Instrument Corporation Spectratrak 620 field transportable quadrupole GC/MS with dimethyl silicone membrane inlet and internal trap/thermal desorber for direct MS operation**

# Field Screening Procedures

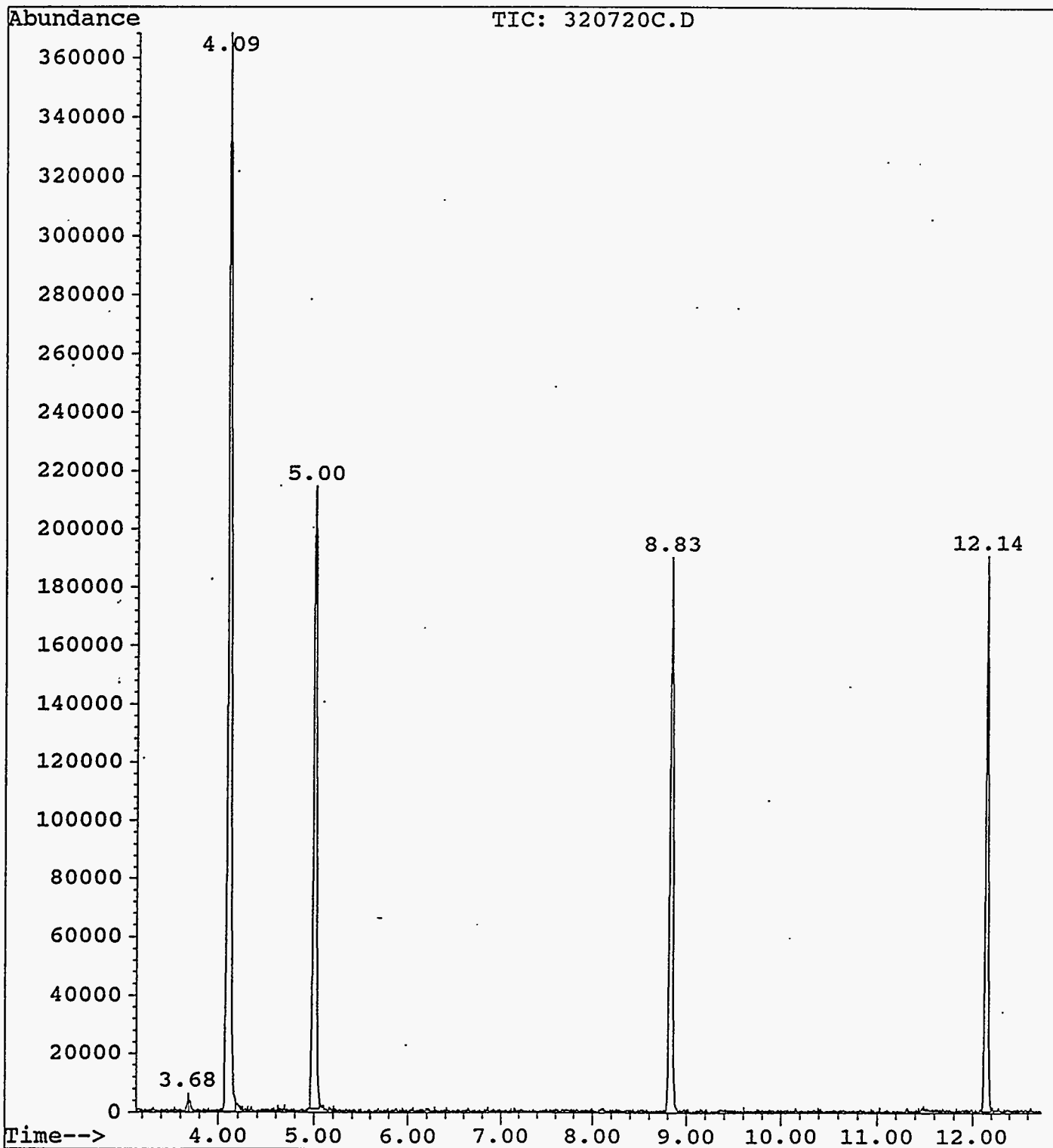
- **Water samples analyzed by headspace method GC/MS**
- **Soil samples preserved in the field with methanol and analyzed by direct purge MS or purge-and-trap MS**
- **Gas samples analyzed by direct injection GC/MS or sample concentration GC/MS**



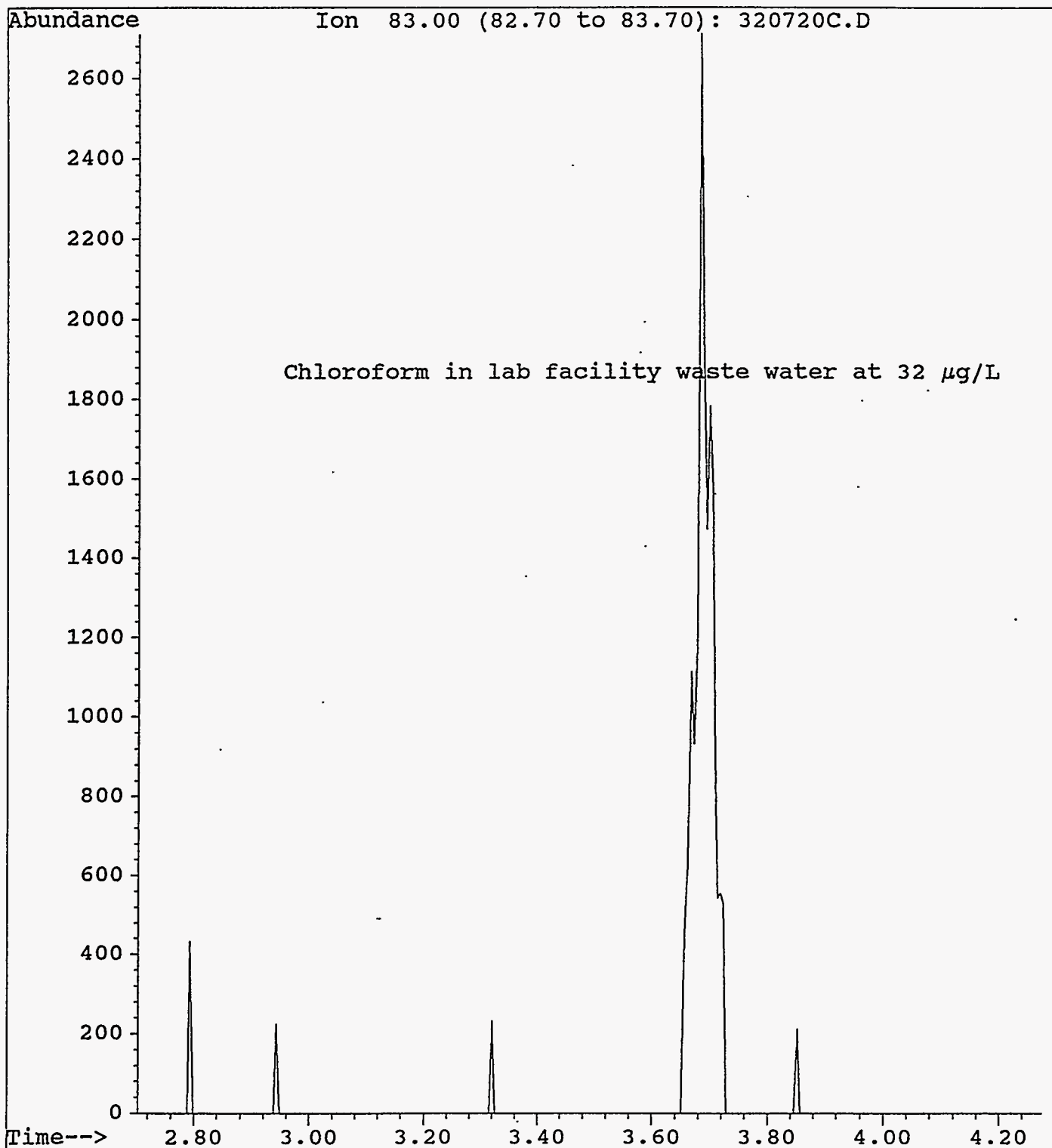
# Headspace GC/MS (Water)

- Samples are collected in 40 ml brown glass VOA vials
- 20-ml water sample is used for analysis aliquot
- Four-component standard mixture in methanol is injected through cap septum. 1,4-difluorobenzene is used as ISD and other three compounds are used as surrogates
- MDL is approximately 1 µg/L for most compounds with full scan from 35 amu to 260 amu
- Lower MDL may be obtained as needed by use of SIM mode
- Analysis time is 10 minutes per sample for analytes up to xylenes on either HP or Viking

File : C:\HPCHEM\1\DATA\320720C.D  
Operator : JCE  
Acquired : 22 Jul 94 6:12 am using AcqMethod VOC  
Instrument : 5971 - In  
Sample Name: 320 Buliding on 7/20/94 at 1128  
Misc Info : 500 ul air HP  
Vial Number: 1



File : C:\HPCHEM\1\DATA\320720C.D  
Operator : JCE  
Acquired : 22 Jul 94 6:12 am using AcqMethod VOC  
Instrument : 5971 - In  
Sample Name: 320 Buliding on 7/20/94 at 1128  
Misc Info : 500 ul air HP  
Vial Number: 1



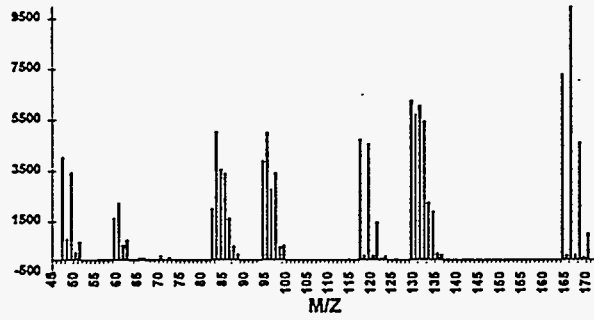
# **Direct Purge MS (Soil or Water)**

- **5 gram soil samples are collected in pretared 40 ml brown glass VOA vial containing 5 ml of methanol**
- **Vial is then reweighed with wet weight used for quantitation**
- **Trifluorotoluene ISD is injected through cap**
- **20 ml of reagent water is added immediately prior to analysis and cap is replaced with AMD direct purge cap with Teflon ball seal**
- **Sample is heated to 70 C on block heater**
- **Sample is purged with helium for 5 minutes over dimethyl silicon membrane inlet with 8 compounds + ISD quantified by full scan analysis using HP MS**
- **Similar procedure may be used with Viking but the addition of a Tenax trap extends analysis time by additional 6 minutes**

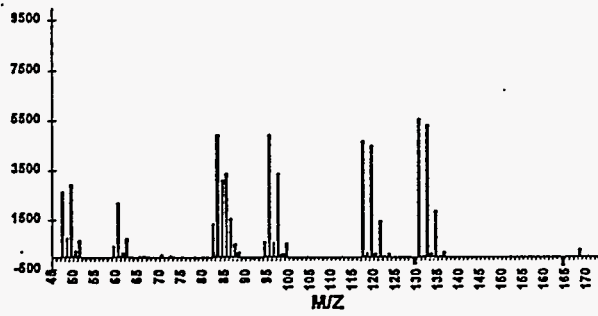
# Direct Purge MS (contd)

- Compounds currently included in method: methylene chloride, chloroform, carbon tetrachloride, TCE, PCE, benzene, toluene, xylenes and trifluorotoluene (TFT) internal standard
- Interspecies interferences 0-3%. TFT does not interfere with any of the 8 analytes studied. Other analytes require interference determination
- MDL for soil is 20 to 40 µg/kg and 4 to 8 µg/L for water
- Linearity verified for at least 4 decades relative to a single point ISD
- HP version of method published in DOE Field Methods Compendium (OS040-Draft)

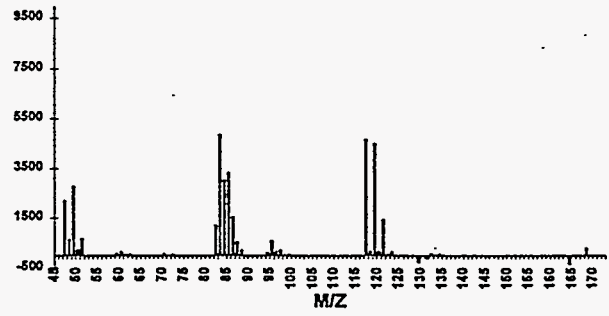
### 5 Component Mixture



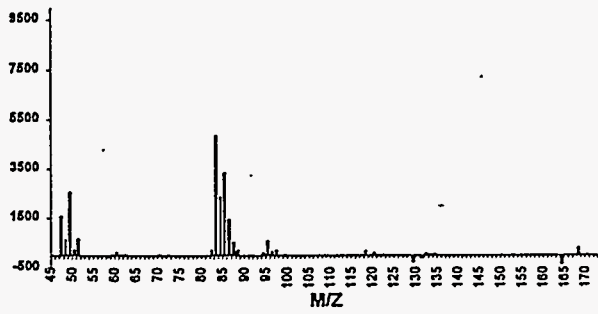
### 5 Component Mixture - PCE



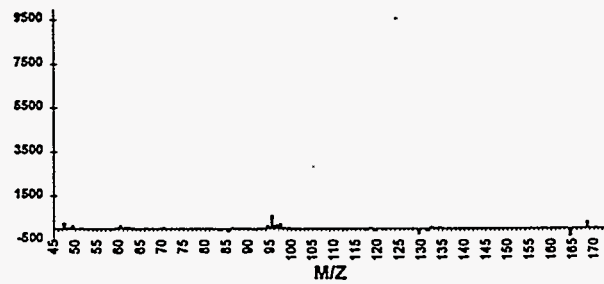
### 5 Component Mixture - PCE, TCE



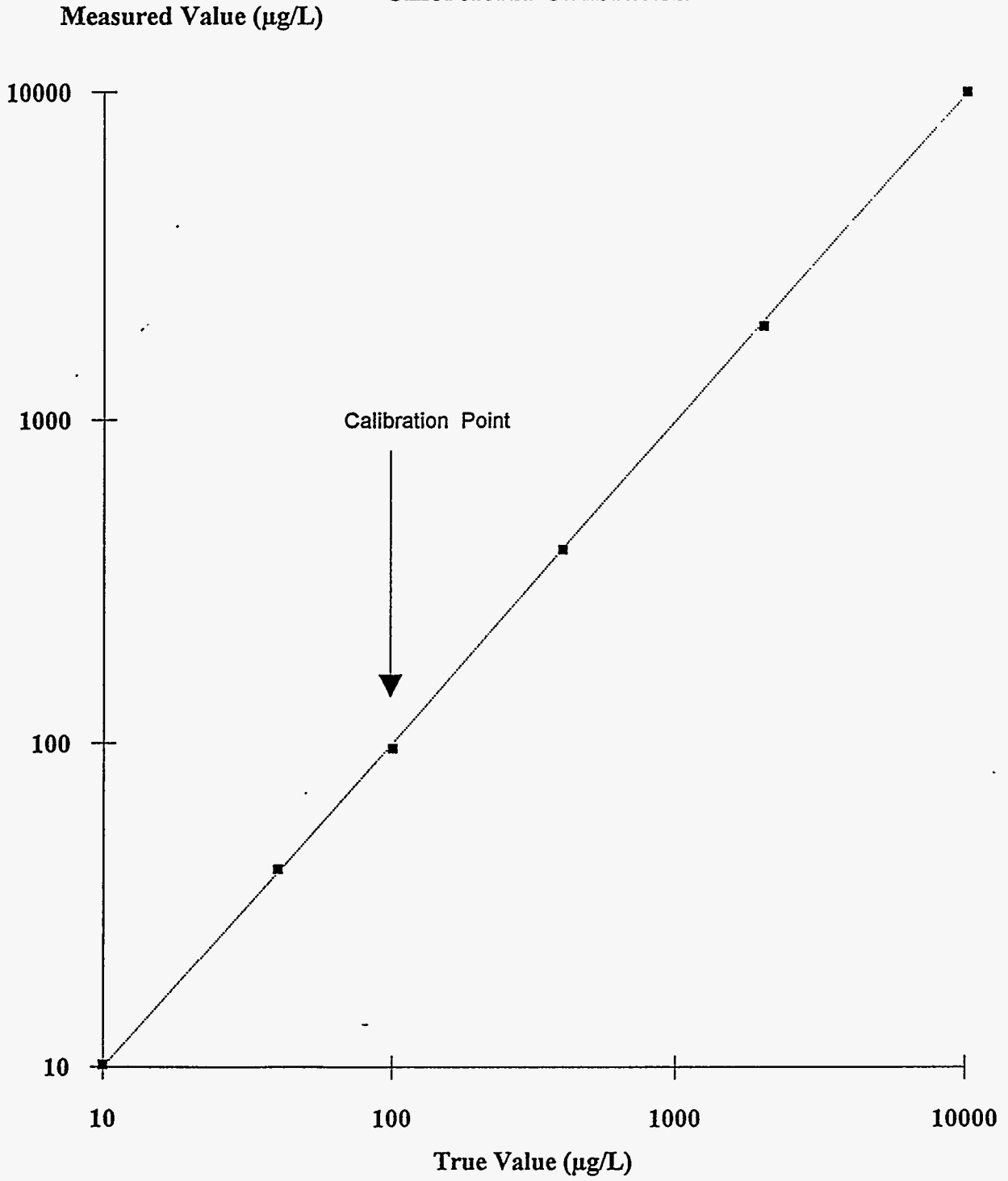
### 5 Component Mixture - PCE, TCE, CCl4



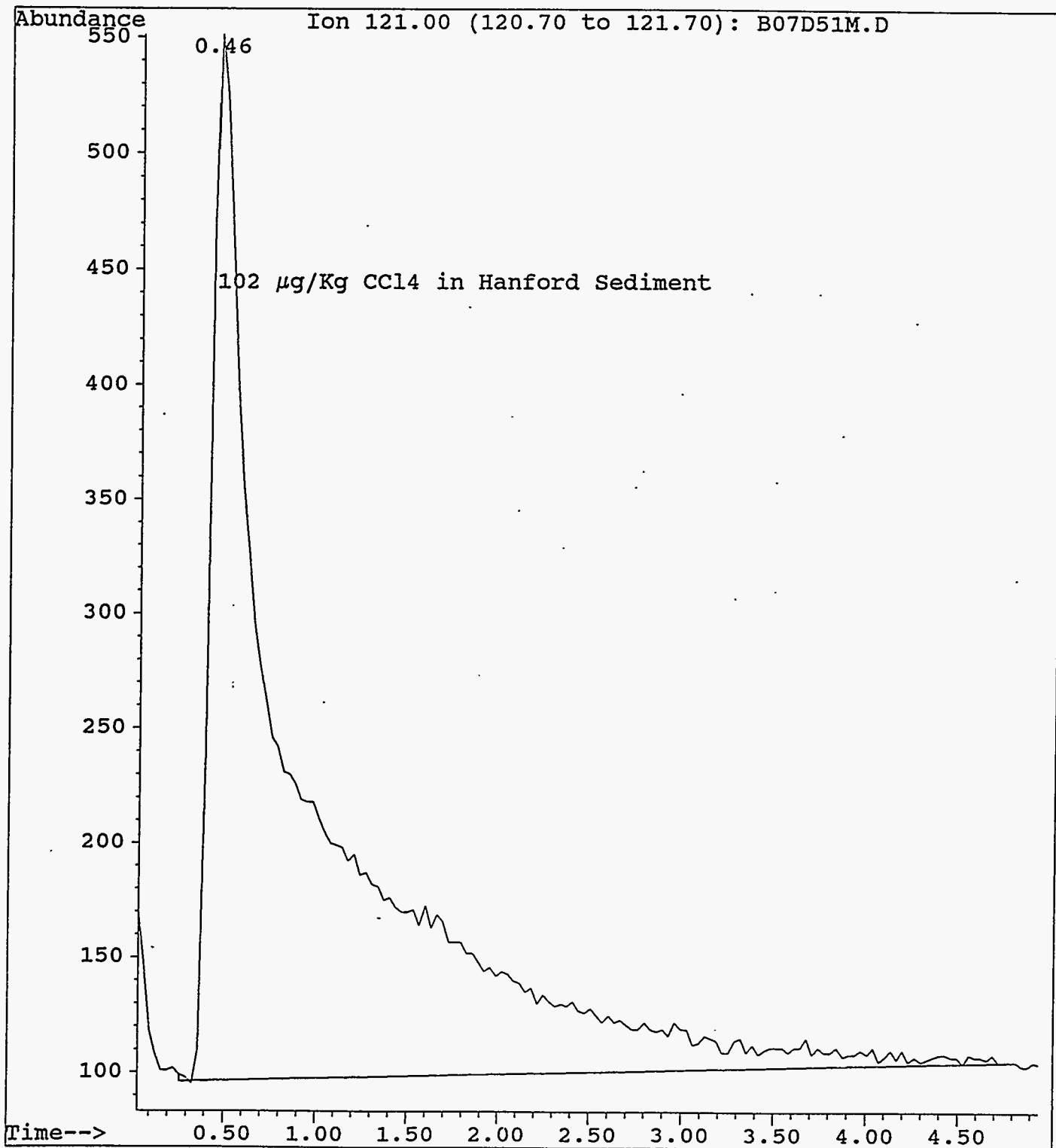
### 5 Component Mixture - PCE, TCE, CCl4, CHCl3, CH2Cl2



# Direct Purge MS Chloroform Calibration

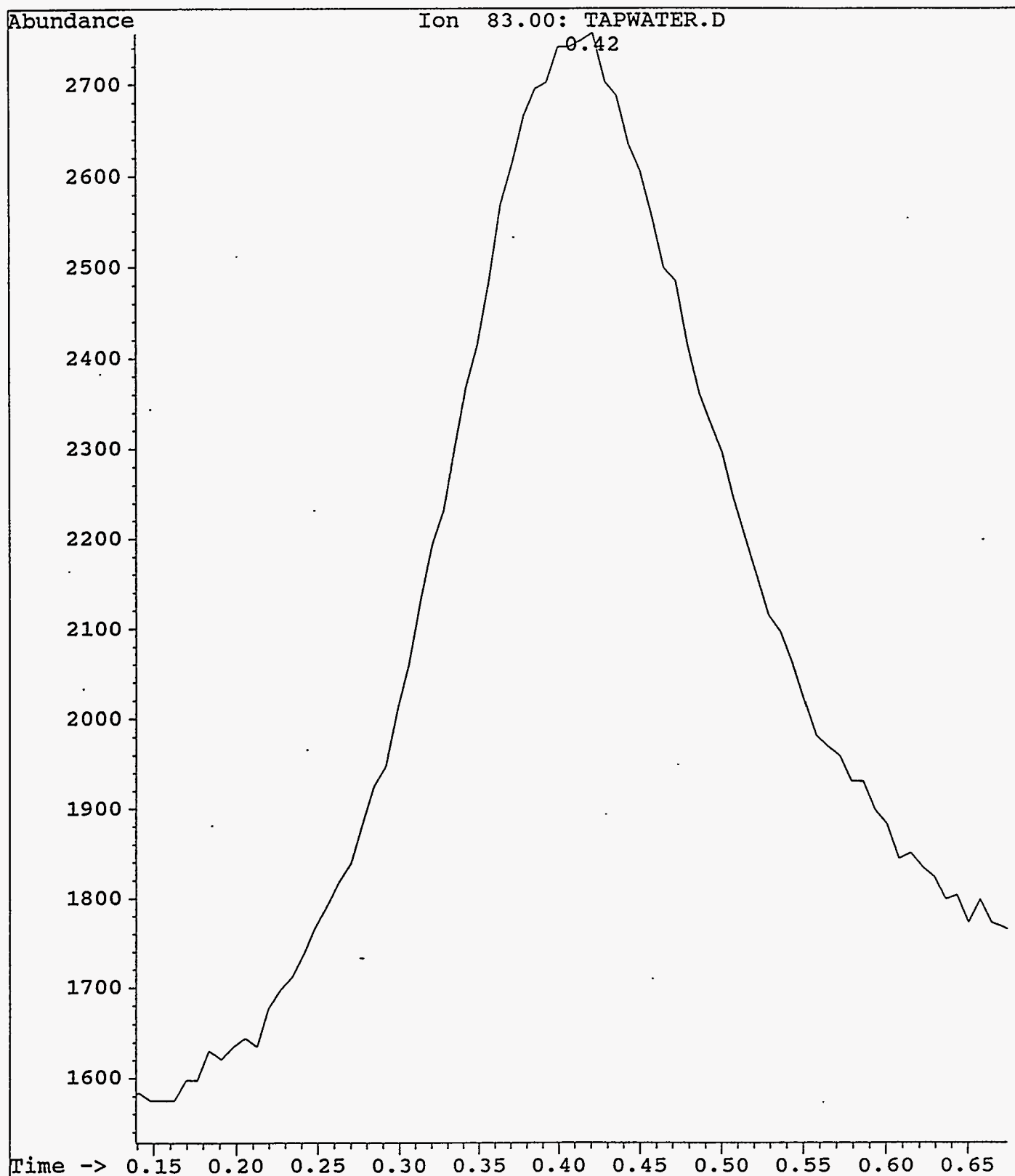


File : C:\HPCHEM\1\DATA2\B07D51M.D  
Operator : JCE  
Acquired : 24 Sep 93 12:34 pm using AcqMethod PURGESIM  
Instrument : 5971 - In  
Sample Name: B0D51 methanol  
Misc Info :  
Vial Number: 1





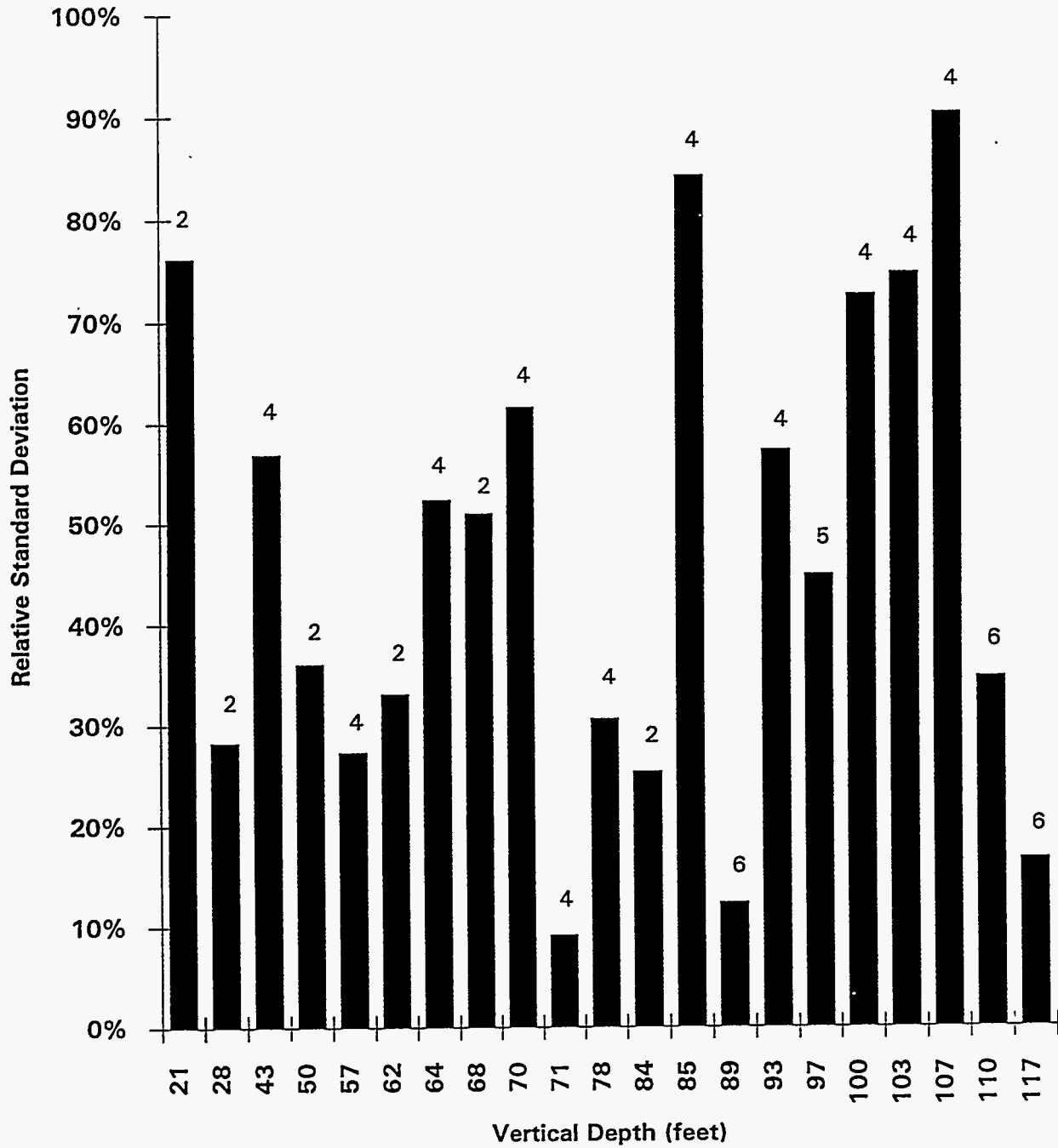
Data File: C:\CHEMPC\DATA\SCONMS\RUN1.R\TAPWATER.D  
Date Acquired: 19 Oct 94 9:16 am  
Operator: JCE  
Sample Name: PNL Sigma 5 Building Tapwater  
Misc Info: 25 mL purged for 5 minutes onto Tenax trap



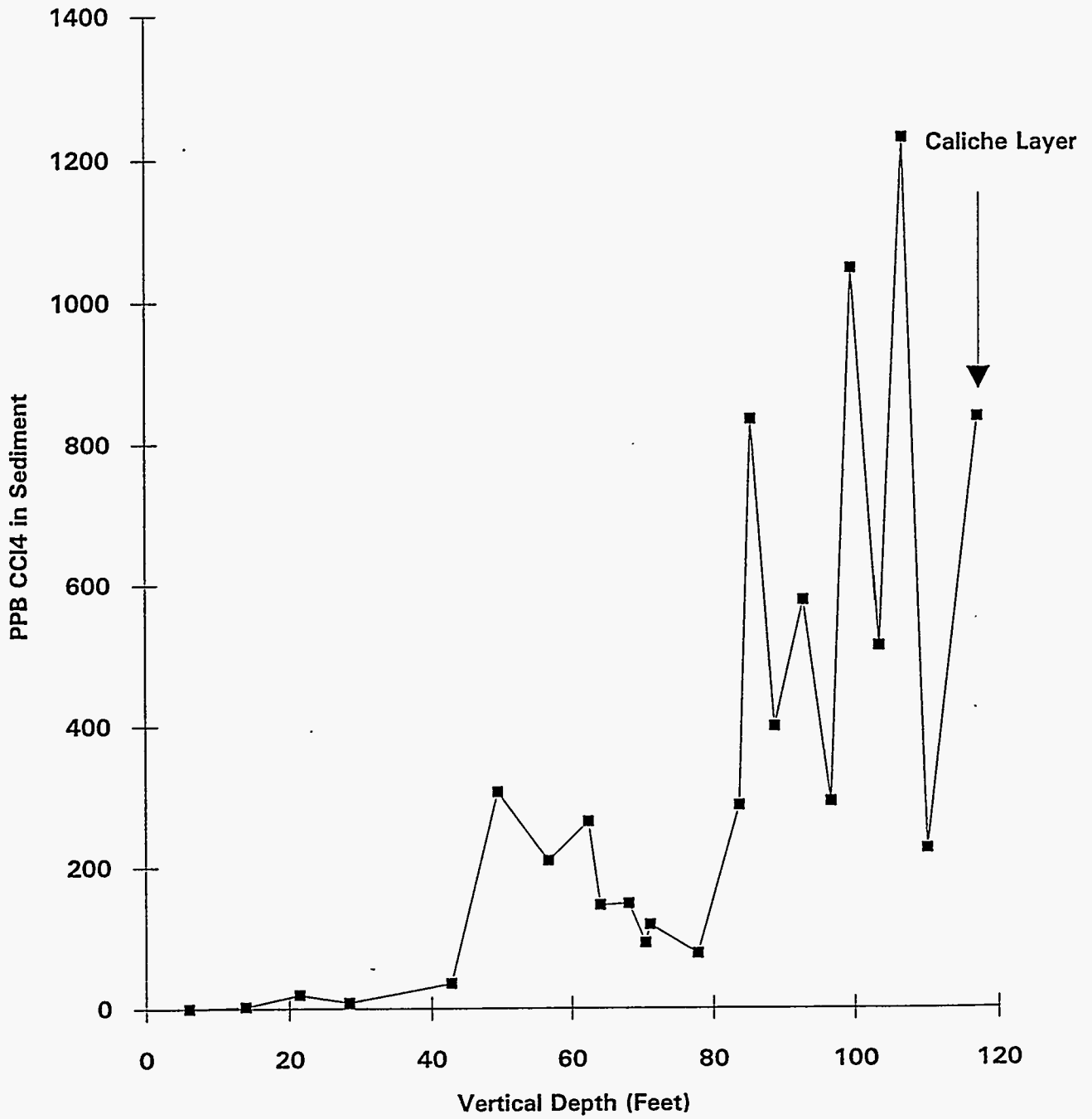
# **Application Example (Soil Analysis)**

- **Soil samples collected by Resonant Sonic drilling in Hanford 200 West Area carbon CCl<sub>4</sub> soil contamination zone; 1000 tons CCl<sub>4</sub> in ground**
- **Drilled at 45-degree angle with samples recovered in Lexan-lined split barrel sampler**
- **Samples collected at vertical depths ranging from 6 to 117 feet with 2 to 6 samples collected at each stop**
- **Samples preserved with methanol in field**
- **Methanol extracts split for analysis by MS and purge-and-trap GC (EPA Method 502.2)**
- **Samples showed only CCl<sub>4</sub> contamination**
- **Agreement was good between MS and GC methods**

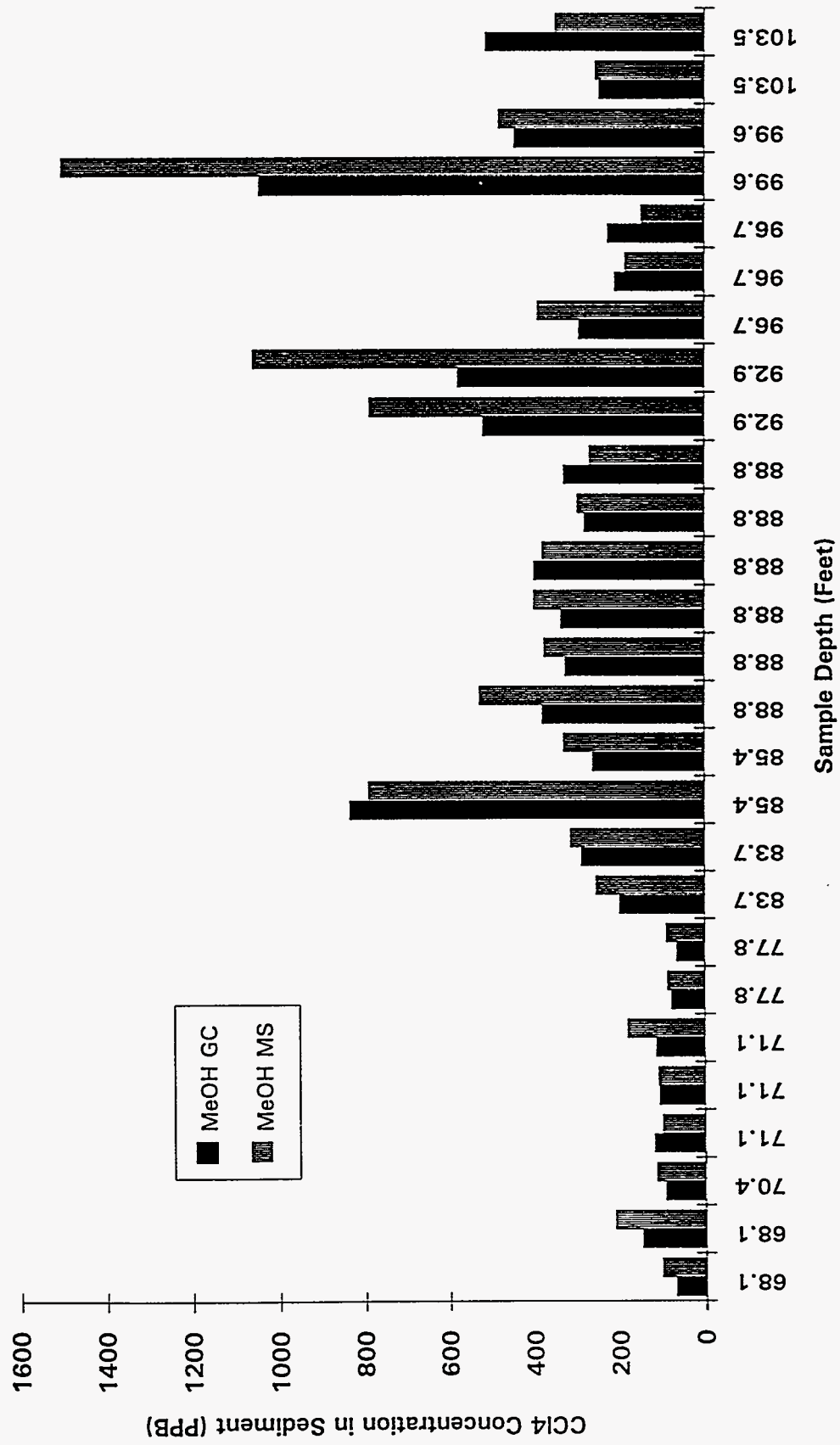
CCl4 in Sediment at 299-W15-223  
Relative Variability



CCl4 in Sediment at Site 299-W15-223  
Maximum Values Plotted



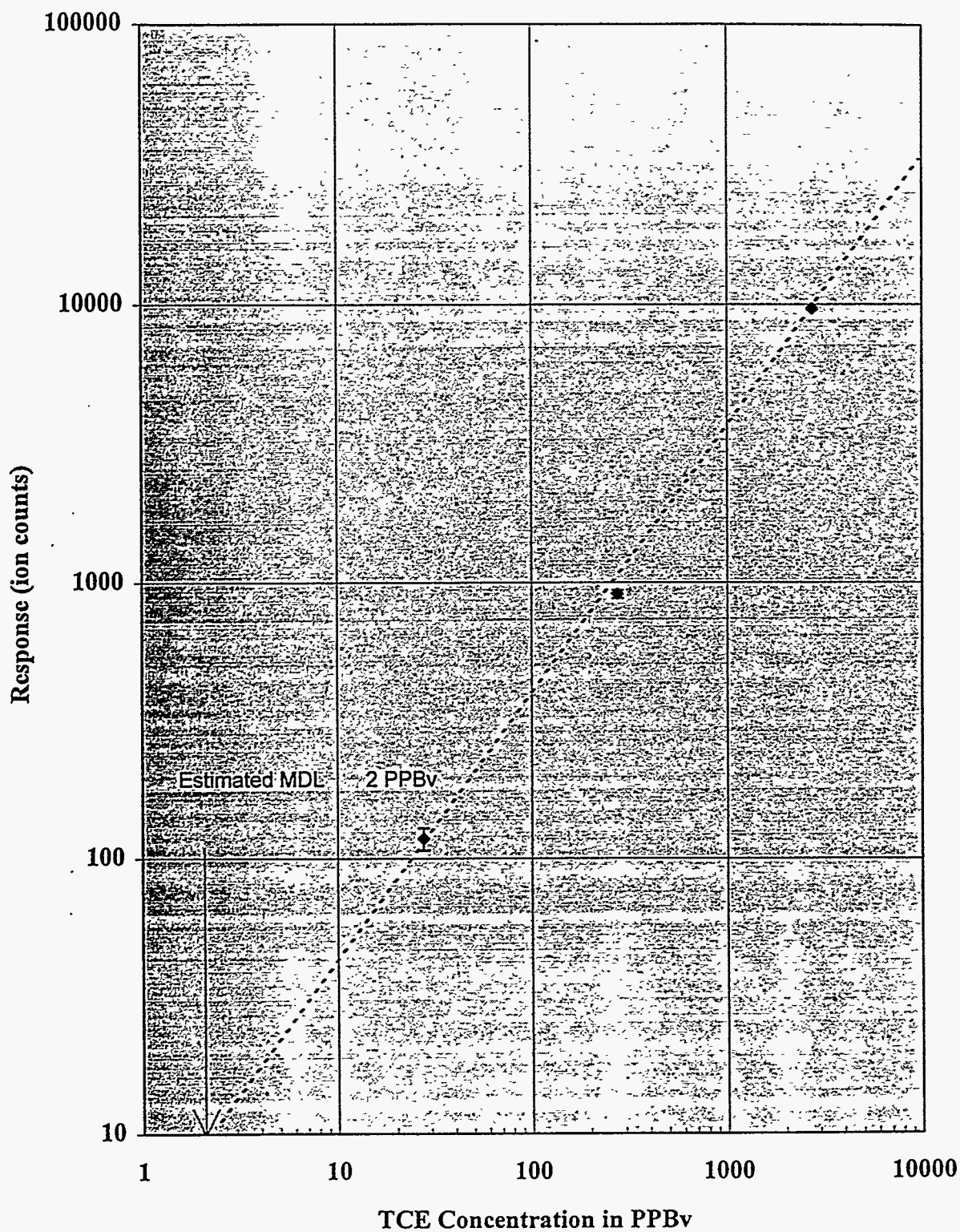
# CCl4 in Sediments at Site 299-W15-223



# Direct Injection GC/MS (Gas)

- Samples collected in Tedlar bags or flowthrough glass bottles
- Samples stored in the dark prior to analysis and analyzed promptly
- Standards prepared from neat materials injected into Tedlar bags followed by secondary dilution
- 500- $\mu$ L air samples are direct injected onto GC column of either HP or Viking system
- Analysis is typically full spectrum to identify unknowns followed by ad hoc rapid SIM analysis for speed and sensitivity
- TCE analysis takes 4 minutes per sample with MDL approximately 2 PPBv

# TCE Vapor Calibration



500  $\mu$ L direct injection; Single ion monitoring on 132 amu. 7:1 split ratio

# **Sample Concentration GC/MS**

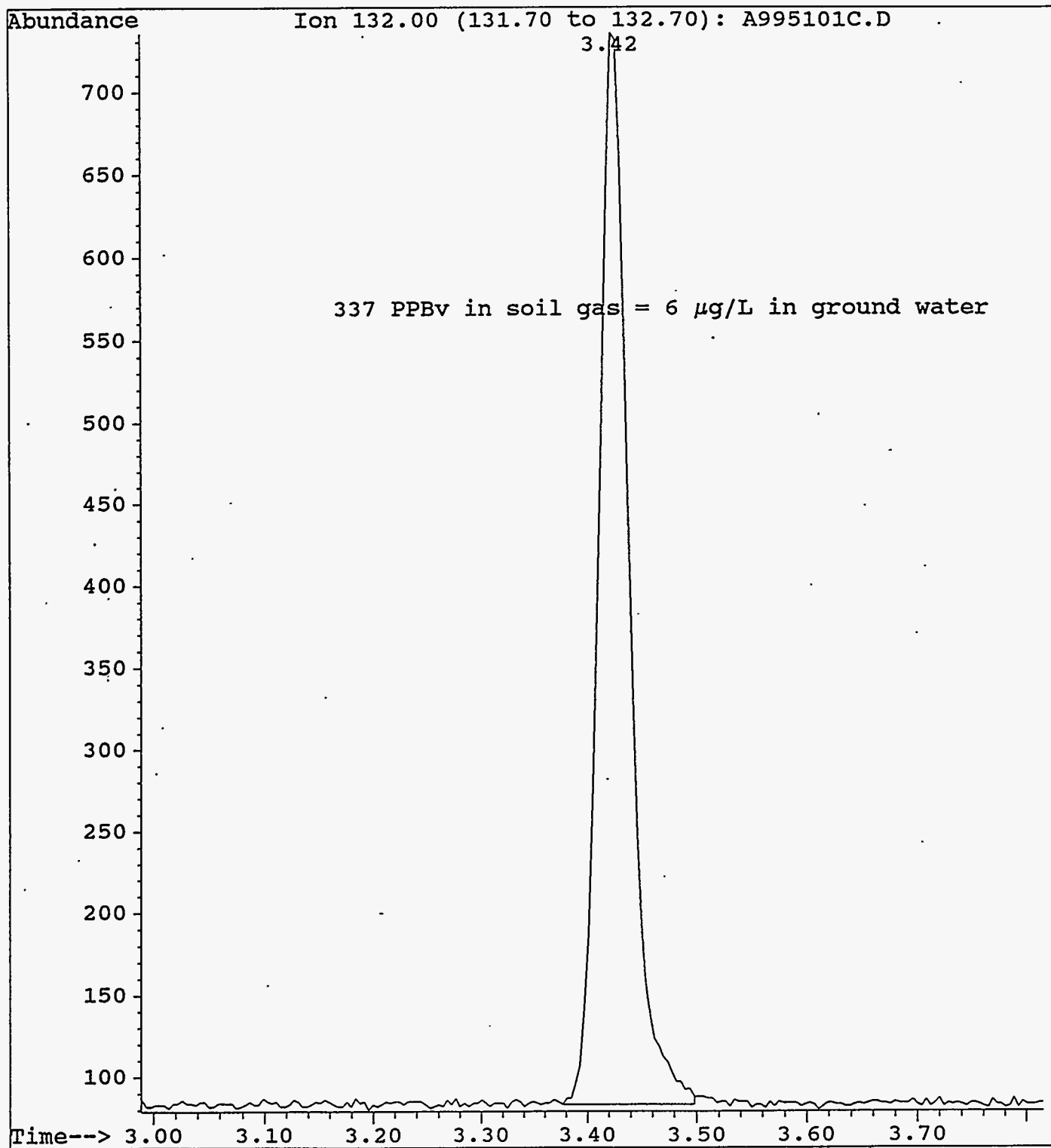
- **Air samples of 200 ml or more collected on Tenax or Supelco 300 carbon sorbent traps using BIOS International Air Pro MP sampling pump with mass flow controller**
- **Tubes desorbed by Viking internal thermal desorber directly onto GC column**
- **Sensitivity of low parts-per-trillion attainable even in full scan mode**
- **Analysis time is 15 to 20 minutes per sample**



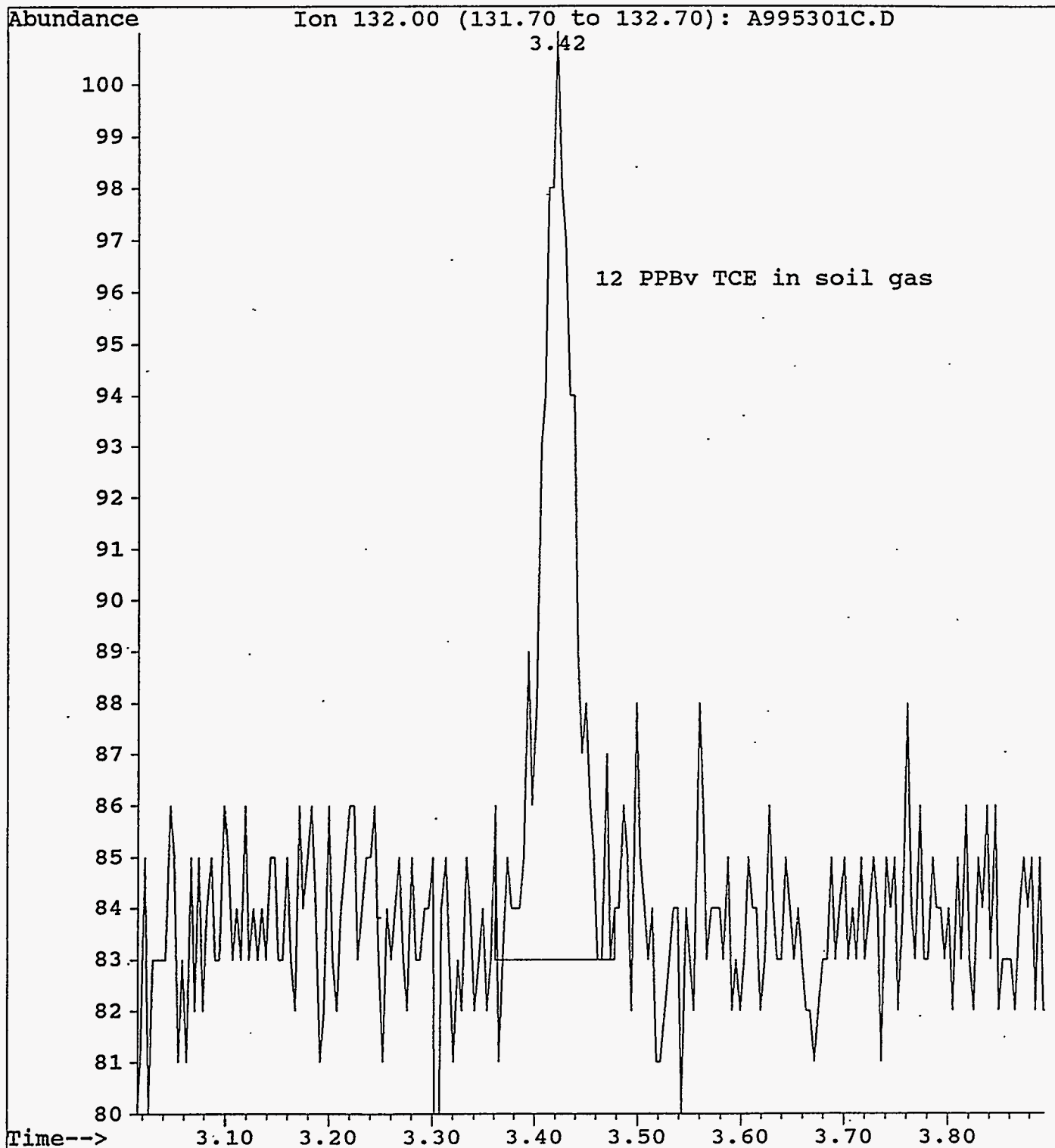
# **Application Example (Soil Gas)**

- **22 soil gas sampling points installed at Hanford Horn Rapids Landfill to track TCE plume originating from offsite source**
- **Sampling points installed by ARA 35 ton cone penetrometer over two-day period; location survey by GPS**
- **Water table at 40 feet; soil gas points installed at depths ranging from 9 to 26 feet**
- **Samples collected and analyzed on same day using direct injection GC/MS on HP**
- **TCE was detected in 12 of the 22 locations over wide area**
- **Sample concentration method will be used on next collection series to obtain better definition of plume**
- **Plume will be monitored by this method for several years to test natural attenuation hypothesis currently in effect in ROD**
- **Soil gas method was found to be more sensitive for detection of TCE than conventional well samples; vertical gradient likely**

File : C:\HPCHEM\1\DATA\A995101C.D  
Operator : JCE  
Acquired : 27 Sep 94 4:33 pm using AcqMethod TCESIM  
Instrument : 5971 - In  
Sample Name: A9951-01 on 9/27/94 at 845  
Misc Info : 500 ul of soil gas  
Vial Number: 1



File : C:\HPCHEM\1\DATA\A995301C.D  
Operator : JCE  
Acquired : 27 Sep 94 3:32 pm using AcqMethod TCESIM  
Instrument : 5971 - In  
Sample Name: A9953-01 on 9/27/94 at 955  
Misc Info : 500 ul of soil gas  
Vial Number: 1



# Conclusions

- **Mass spectrometry methods are a valuable addition to either rapid laboratory screening or under proper conditions field screening activities**
- **Significant method development is needed for individual applications**
- **MS identification capability can be of great value in field investigations**
- **Direct MS is very rapid but should be limited to very simple combinations of analytes or well studied mixtures; situation can be improved with PCA software**
- **High cost of MS instrumentation remains a major problem; for many applications field portable GC is more cost effective**