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

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

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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

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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

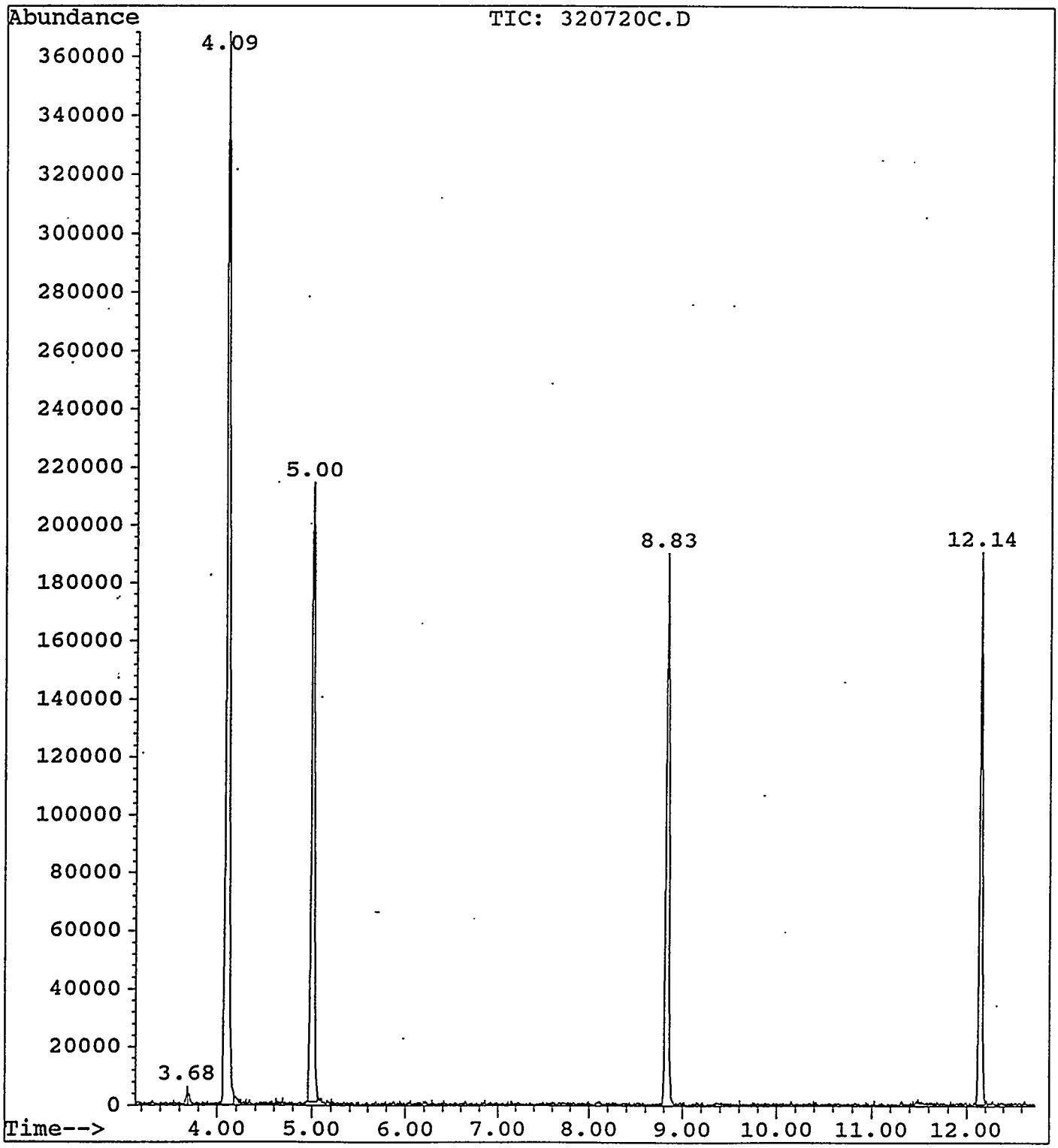
Field Screening Procedures

- 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



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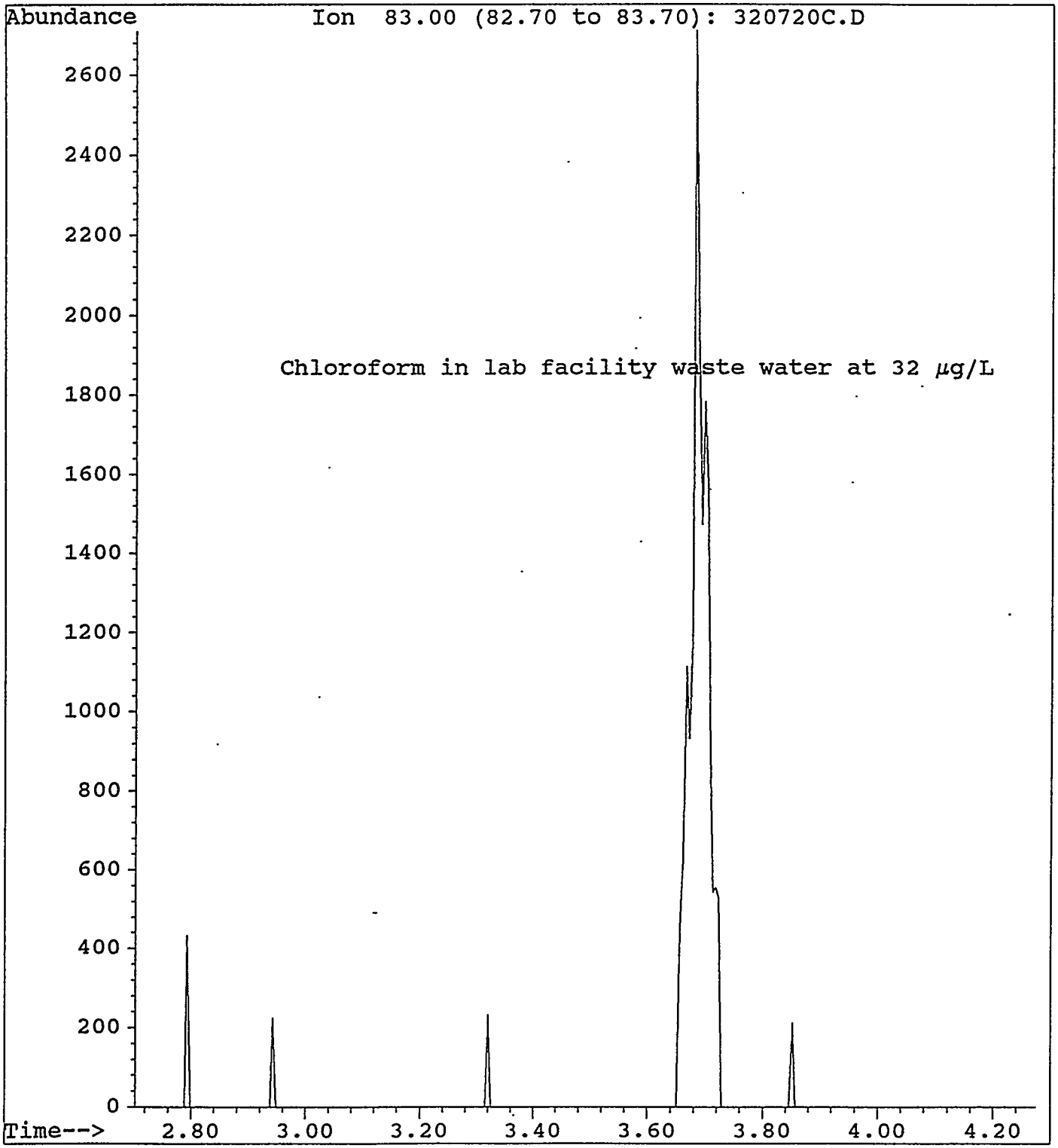


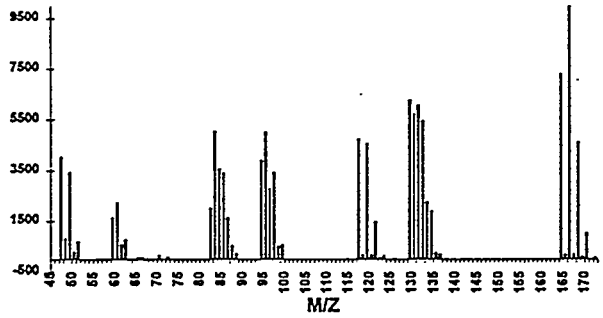
Direct Purge MS (Soil or Water)

- 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

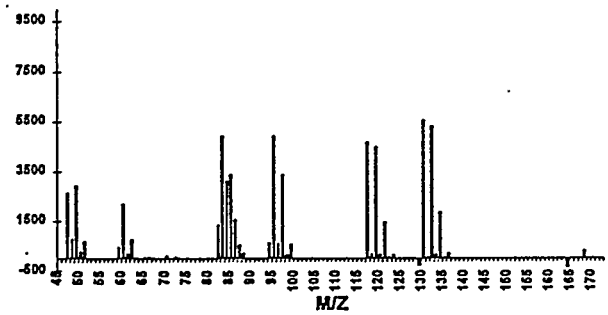
Direct Purge MS (contd)

- 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)

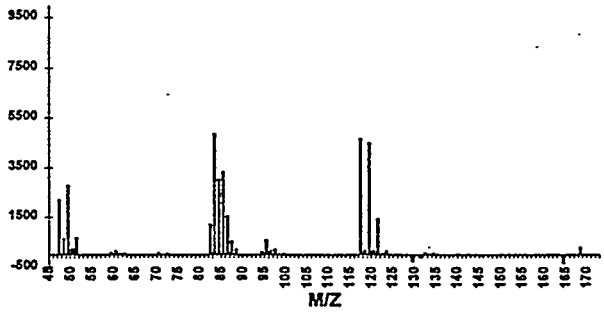
5 Component Mixture



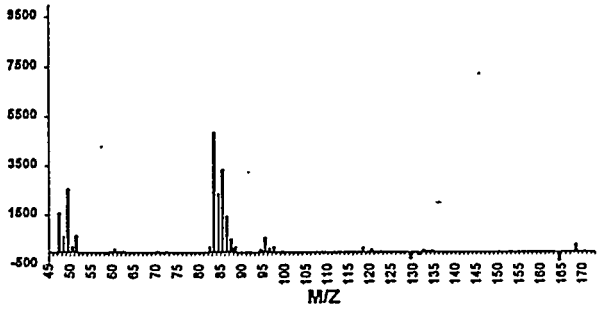
5 Component Mixture -PCE



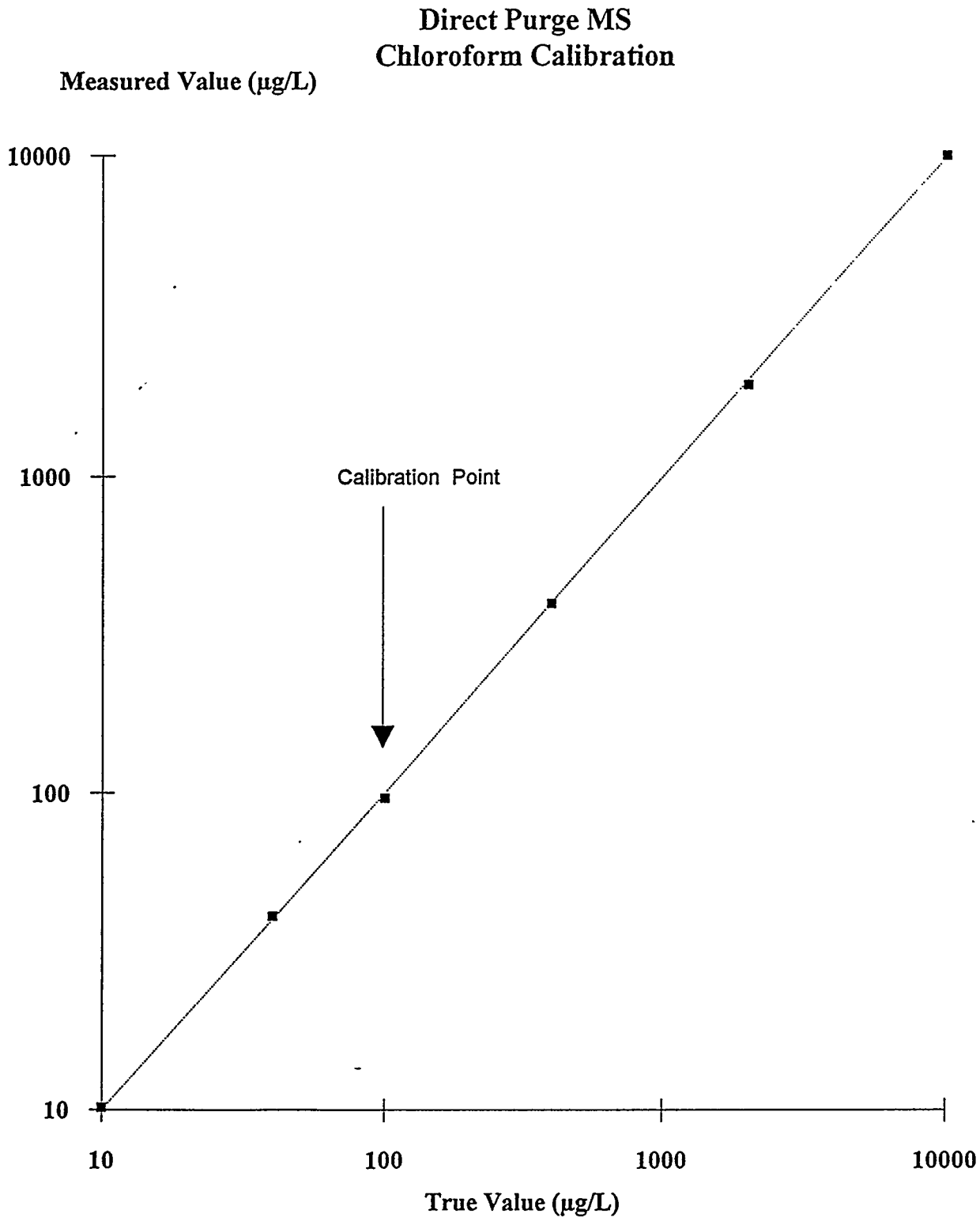
5 Component Mixture - PCE, TCE



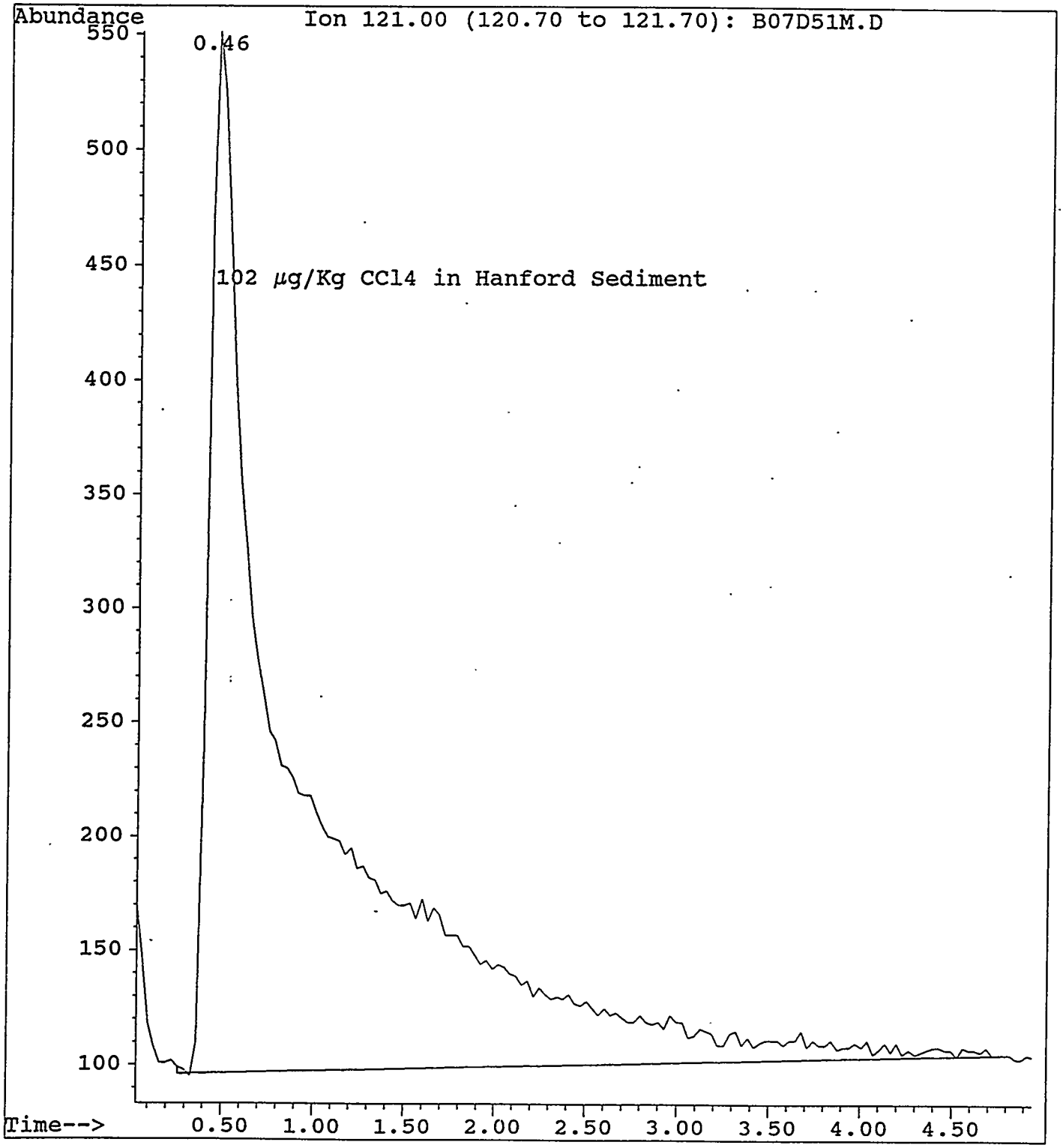
5 Component Mixture - PCE, TCE, CCl4



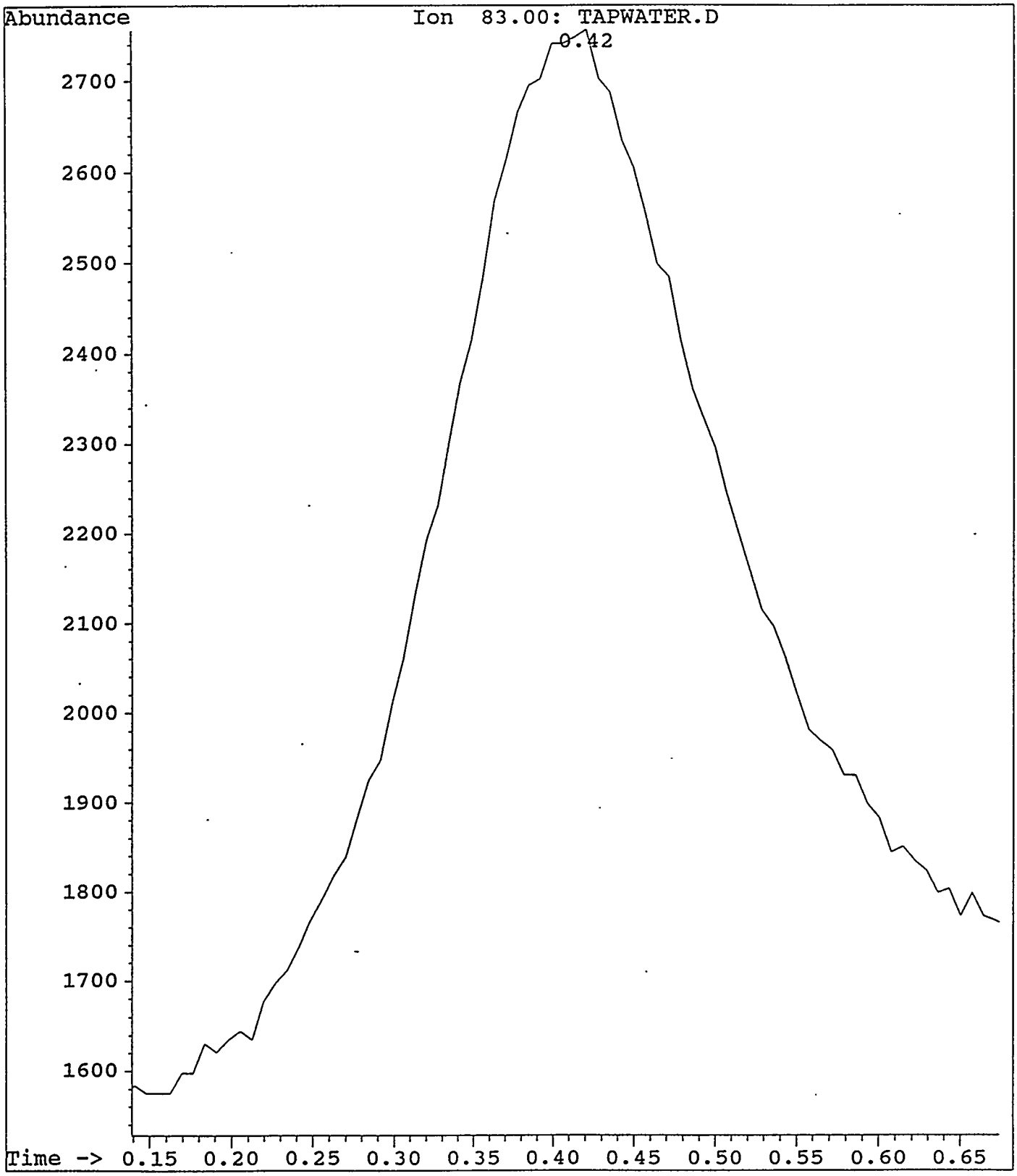
5 Component Mixture - PCE, TCE, CCl4, CHCl3, CH2Cl2


Direct Purge MS
Chloroform Calibration
Measured Value (µg/L)
10000
1000
100
10
Calibration Point
10
100
1000
10000
True Value (µg/L)

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



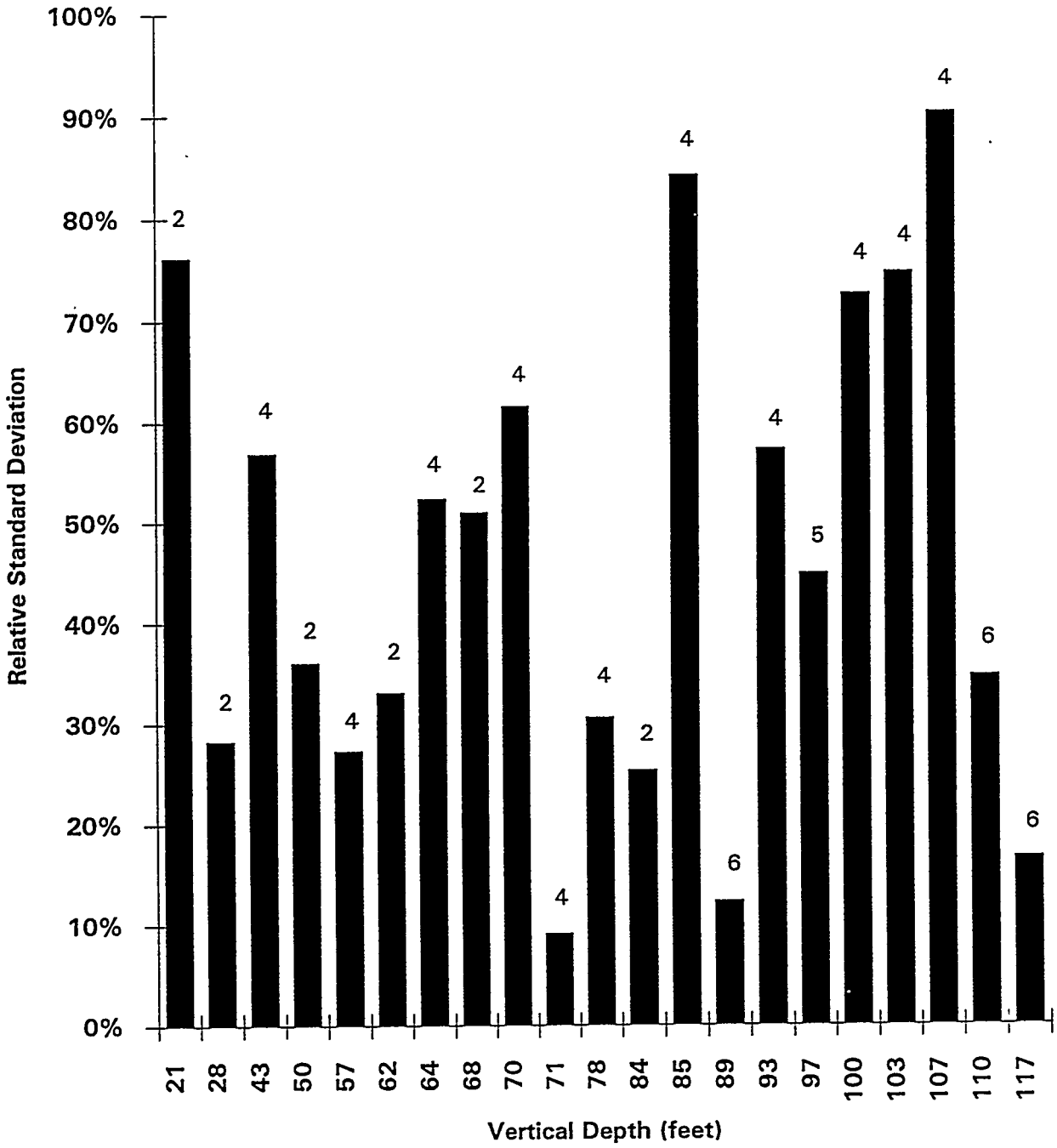
Data File: C:\CHEMPC\DATA\SCONMS\RUN1.R\TAPWATER.D
Date Acquired: 19 Oct 94 9:16 am
Operator: JCE
Sample Name: PNL Sigma 5 Building Tapwater
Misc Info: 25 mL purged for 5 minutes onto Tenax trap

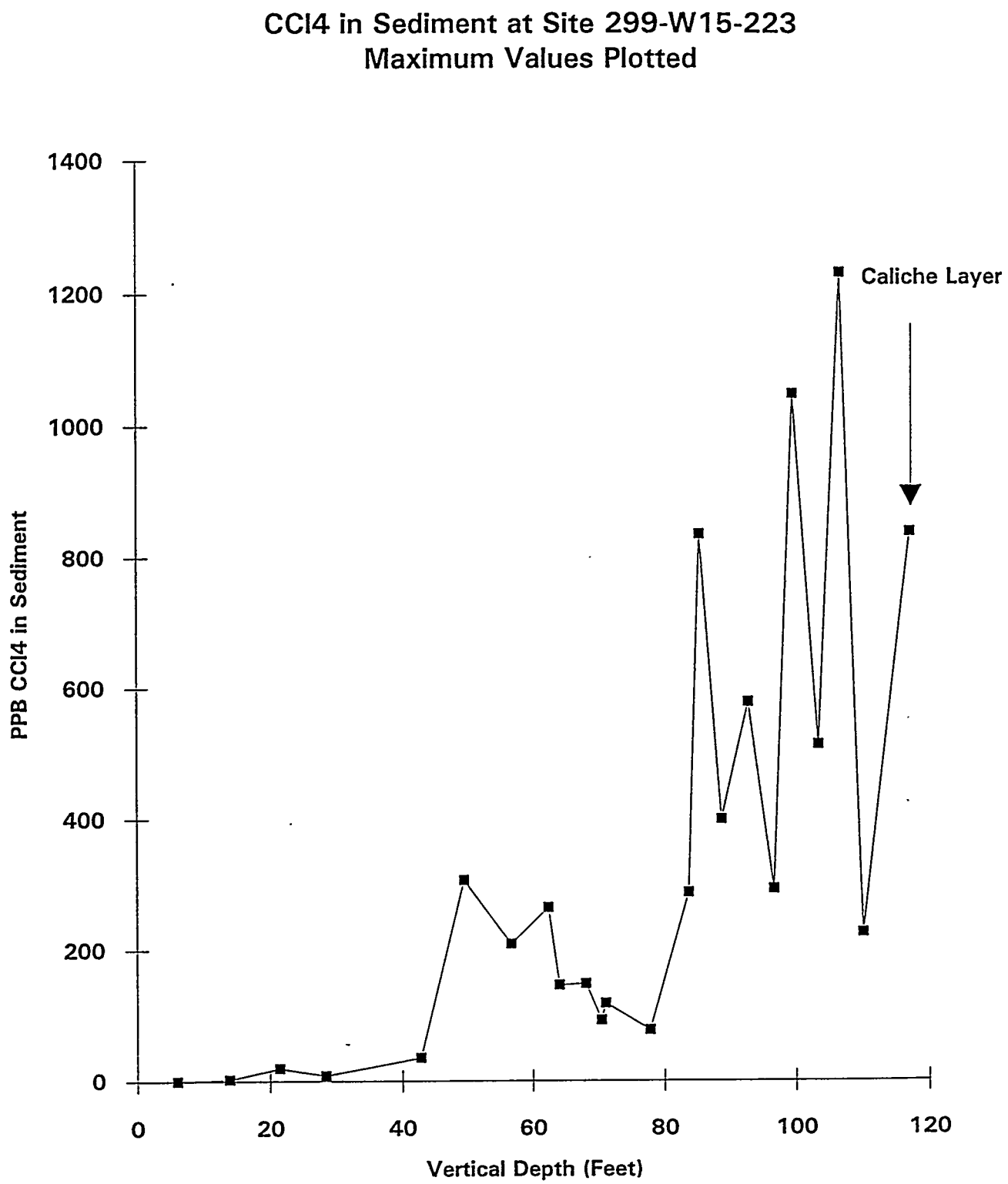


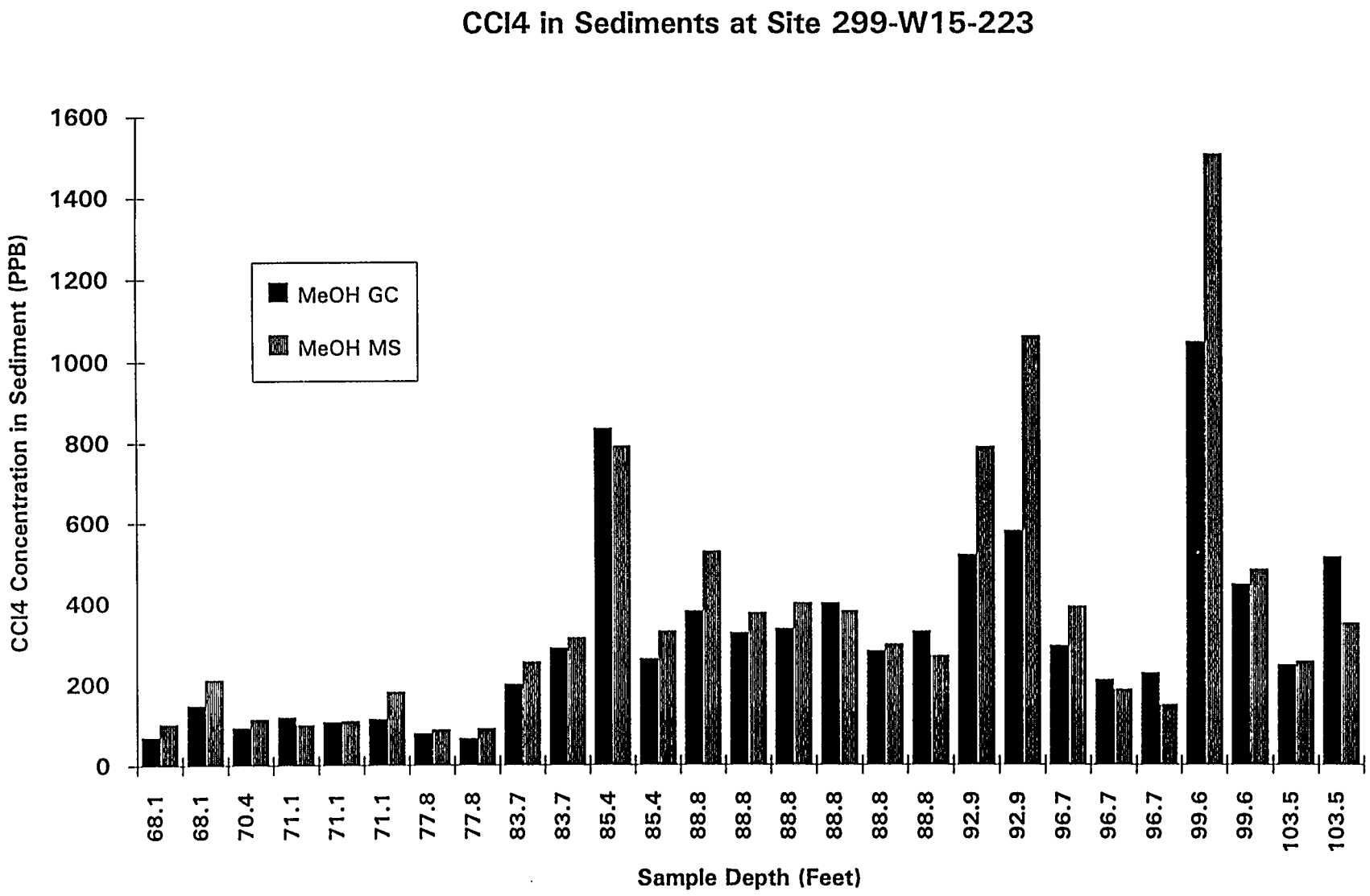
Application Example (Soil Analysis)

- Soil samples collected by Resonant Sonic drilling in Hanford 200 West Area carbon CCl4 soil contamination zone; 1000 tons CCl4 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 CCl4 contamination
- Agreement was good between MS and GC methods

CCl4 in Sediment at 299-W15-223
Relative Variability



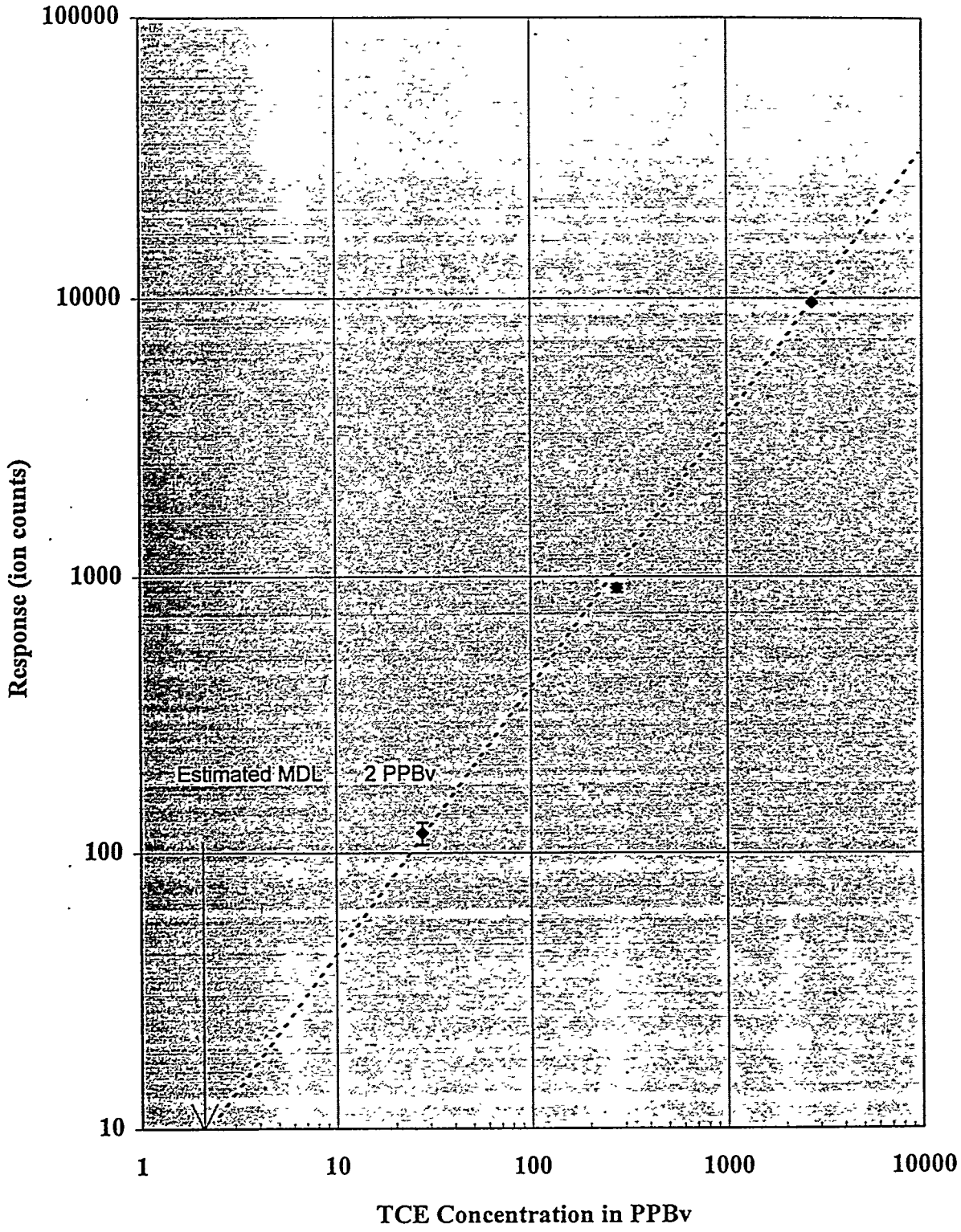

CCl4 in Sediment at Site 299-W15-223
Maximum Values Plotted
Caliche Layer
PPB CCl4 in Sediment
1400
1200
1000
800
600
400
200
0
0
20
40
60
80
100
120
Vertical Depth (Feet)


CCl4 in Sediments at Site 299-W15-223
CCl4 Concentration in Sediment (PPB)
1600
1400
1200
1000
800
600
400
200
0
MeOH GC
MeOH MS
68.1
68.1
70.4
71.1
71.1
71.1
77.8
77.8
83.7
83.7
85.4
85.4
88.8
88.8
88.8
88.8
88.8
88.8
92.9
92.9
96.7
96.7
96.7
99.6
99.6
103.5
103.5
Sample Depth (Feet)

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-µL 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 µL direct injection; Single ion monitoring on 132 amu. 7:1 split ratio

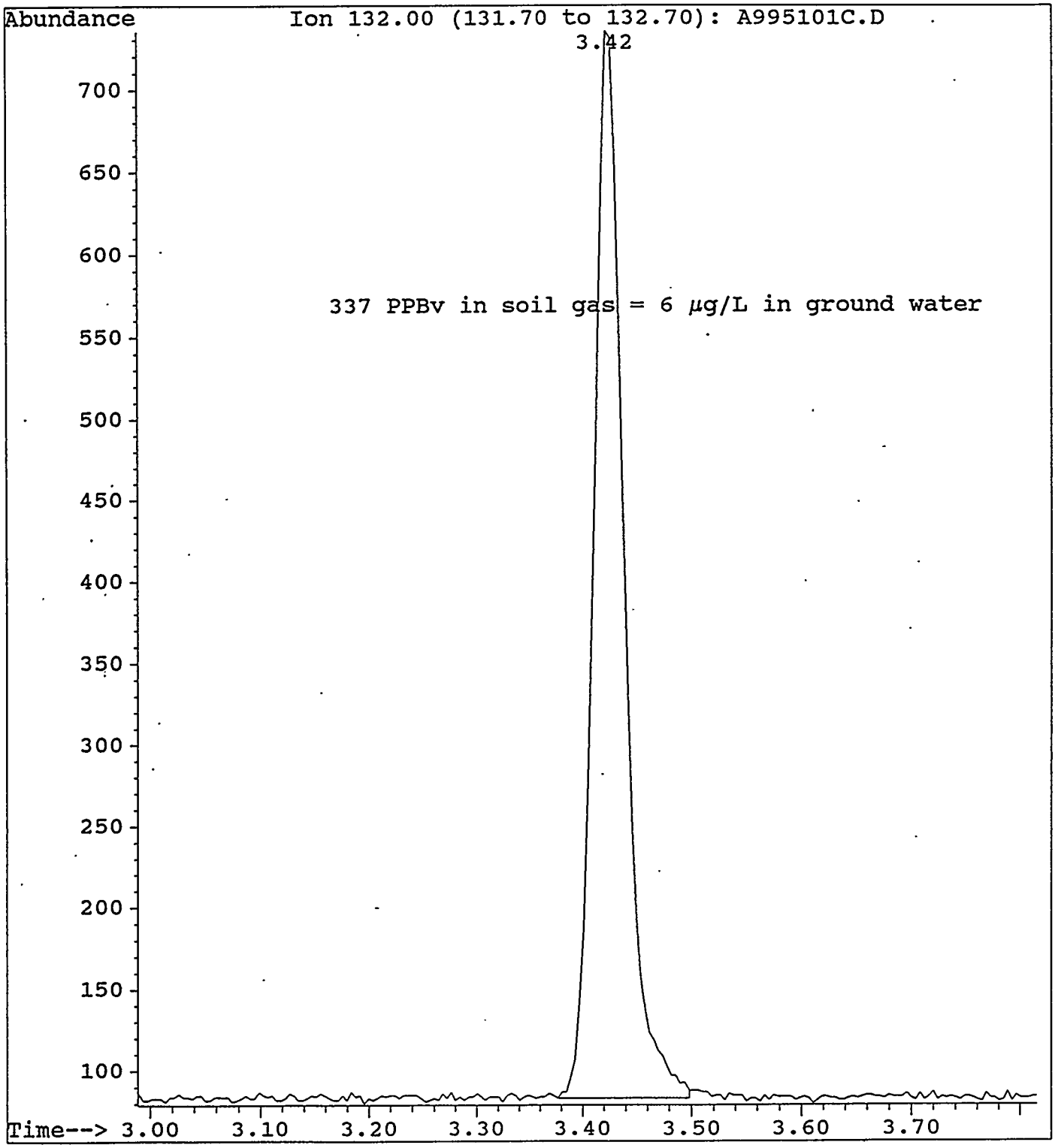
Sample Concentration GC/MS

- 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

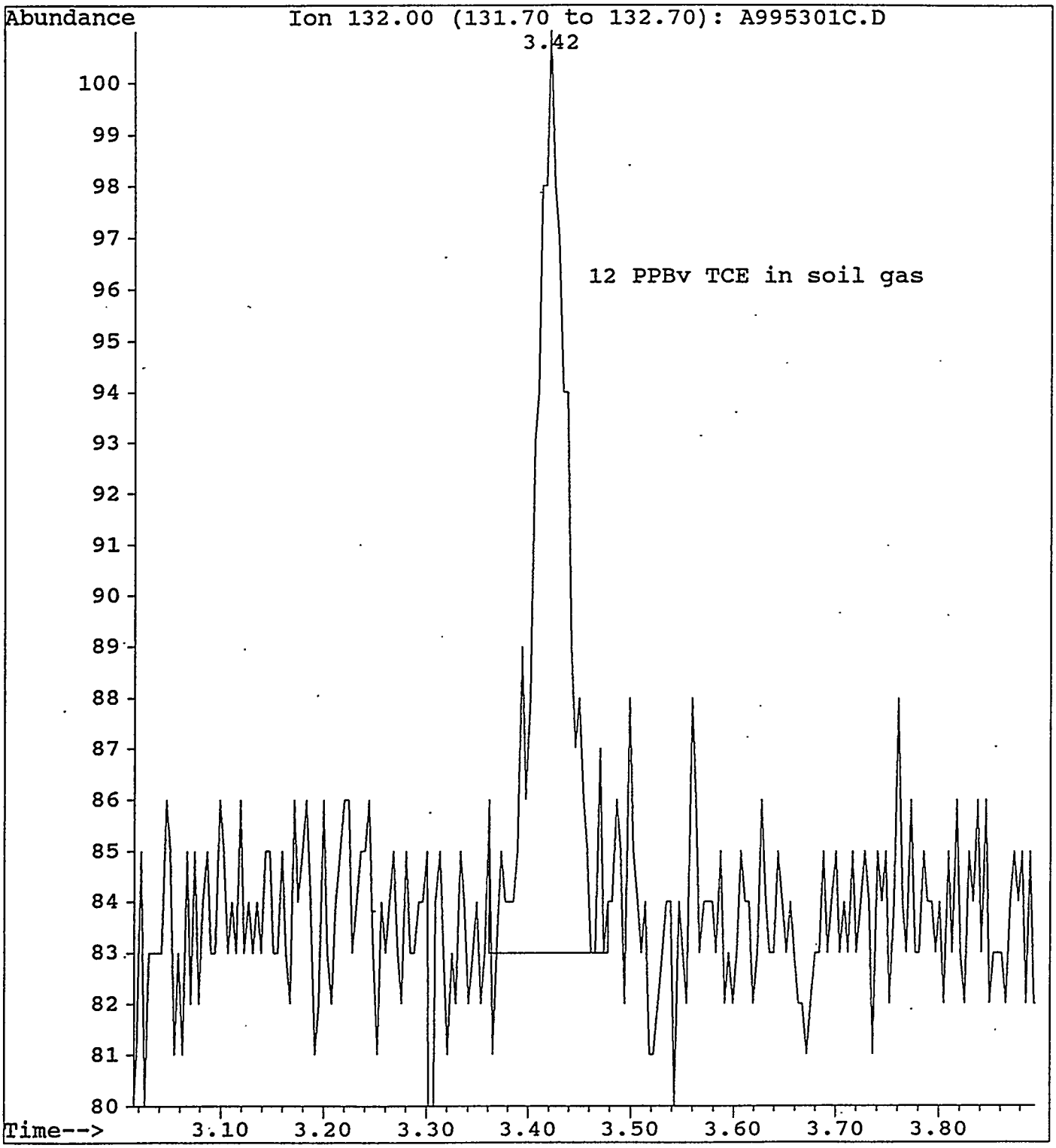
Application Example (Soil Gas)

- 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 sppectrometry 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