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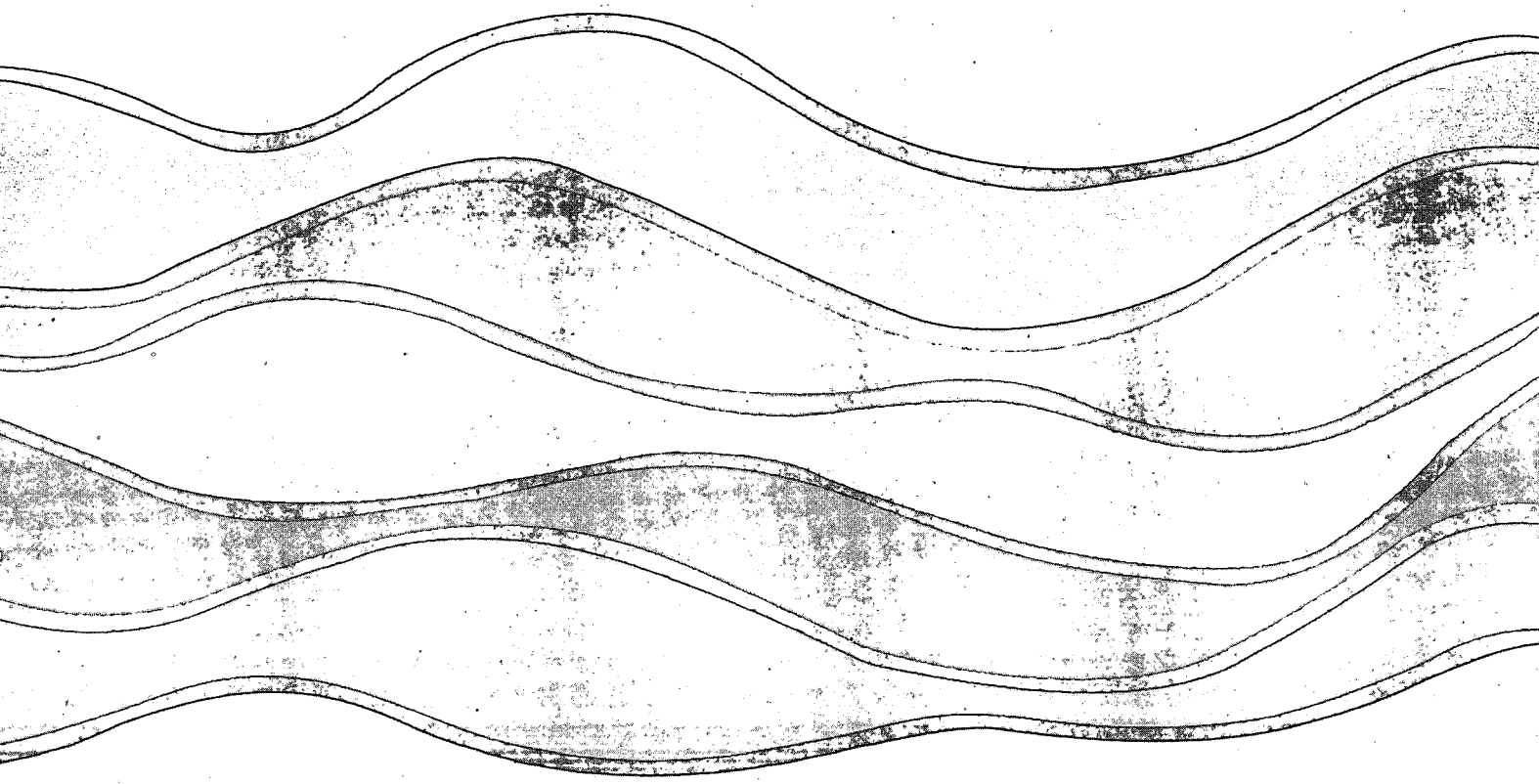

PRACTICAL ANALYTICAL CHEMISTRY FOR HAZARDOUS WASTE SITE INVESTIGATIONS

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NWRI CONTRIBUTION 90-155

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Management perspective

This is an introductory chapter to a book entitled " Ground-Water Contamination at Hazardous Waste Sites: Analysis and Interpretation". It describes briefly the analytical techniques used by chemists in analysing hazardous wastes samples. The emphasis is placed on organic compounds since in the vast majority of cases they pose the main threat to aquifers. Since most hydrogeologists and environmental engineers use the services of contract laboratories for their analytical needs, the relationship with laboratories and the need for strict quality control is also emphasized. Finally the case of suspected ground-water contamination in Newcastle, New Brunswick, is described, where the perceived problem rested entirely on analytical chemistry for its resolution. This report and in fact the whole book should be widely distributed within Environment Canada as it may serve as a reference to environmental engineers and scientist involved in hazardous waste site investigation.

Perspective-gestion

Ceci est le premier chapitre d'un livre intitulé: " Ground-Water Contamination at Hazardous Waste Sites: Analysis and Interpretation". Les techniques d'analyse utilisées par les chimistes pour les déchets dangereux y sont décrites sommairement. Comme la plupart des problèmes de contamination des aquifères sont dus aux composés organiques, on y met une plus grande emphase. Puisque la plupart des hydrogéologues et ingénieurs en environnement utilisent les services de laboratoires commerciaux, les relations avec ces laboratoires et les problèmes de contrôle de la qualité sont discutés en détail. Enfin un cas-type, celui de Newcastle, N.B., où la résolution des problèmes appréhendés reposait entièrement sur l'analyse chimique. Ce rapport et en fait le livre entier pourra servir de référence aux ingénieurs et scientifiques d'Environnement Canada impliqués dans les études de site de déchets dangereux.

Abstract

This chapter describes briefly the analytical techniques used by chemists in analysing hazardous wastes samples. The emphasis is placed on organic compounds since in the vast majority of cases they pose the main threat to aquifers. The main techniques described are GC-MS, GC and HPLC with a mention of more novel hyphenated techniques. Since most hydrogeologists and environmental engineers use the services of contract laboratories for their analytical needs, the relationship with laboratories and the need for strict quality control is also emphasized. Finally a case study is described where the perceived problem rested entirely on analytical chemistry for its resolution.

Résumé

Ce chapitre décrit les techniques d'analyse utilisées par les chimistes pour les déchets dangereux. Comme la plupart des problèmes de contamination des aquifères sont dus aux composés organiques, on y met une plus grande emphase. Les principales techniques décrites sont les CG, CG-SM et CLHP, ainsi qu'une brève mention des techniques combinées. Puisque la plupart des hydrogéologues et ingénieurs en environnement utilisent les services de laboratoires commerciaux, les relations avec ces laboratoires et les problèmes de contrôle de la qualité sont discutés en détail. Enfin un cas-type, où la résolution des problèmes appréhendés reposait entièrement sur l'analyse chimique est décrit.

1.0 Introduction

Many treatises have been written on the topic of aqueous analytical chemistry, but most of them are usually far too comprehensive for the user of analytical results or are silent on how to interpret analytical data produced by others.

Unfortunately most laboratory clients, i.e. hydrogeologists and environmental engineers, are not given the necessary academic background to understand the jargon that analytical chemists use. Most introductory courses are long on nomenclature, and short on practical information for groundwater contamination investigators. This chapter will cover nomenclature in a different way: just know enough to allow the practioners to distinguish between compounds and to recognise synonyms. Secondly, this chapter will attempt to provide insight into the behavior of a component in the subsurface. Finally, advice on field methods of sampling, preservation and analysis will be provided.

The analytical chemical techniques will be described not for the operator of analytical instruments, but more from the viewpoint of the user. Therefore more emphasis will be placed on the output and the understanding of the different level of confidence which may be attached to lab reports. The largest problems usually arise not from what is written down, but from what is not. Assumptions are often the source of misunderstandings: the quality of the interaction with laboratory personnel is often key to the success in a groundwater investigation.

An example of a field investigation will be described to illustrate the importance of adequate analysis in hazardous wastes investigations. A glossary of terms is provided at the end of the chapter for quick reference. Words included in it are highlighted in the text by an asterisk.

2. Laboratory Selection

Most hydrogeologists will have to deal with a contract laboratory when investigating a site. How can one choose? This section will describe a few indicators which may be used in the selection of a laboratory that will answer specific needs of the hazardous waste site investigator.

2.1 Interaction with the laboratory personnel.

While suitable analytical instrumentation and adequate facilities are obviously an essential component of a successful laboratory, the personnel will often make the difference between the average and the superior facility. It is important to be able to discuss the sampling program with the managers, expose specific needs and be satisfied that the laboratory personnel will be attentive to them. It should be possible to meet the personnel or at least be informed of the individuals involved and of their qualifications (both academic and experience).

The laboratory should have examples of their reports, be willing to do a blind sample* and share their round-robin* results. A protocol should be established in case the results are not as expected. Will a second analysis be performed at no extra cost to the client? A comprehensive discussion with several laboratory managers prior to awarding the contract is therefore the first step in any site investigation. It is important to remember that sampling groundwater is expensive and often there are time constraints that preclude resampling.

2.2 How long will it take for the samples to be processed ?

The best labs are often the busiest. It is therefore important to discuss with the laboratory how the samples fit in their schedule and what priorities your samples will receive. Will they take a contract with penalties for late reports, or do they charge a premium for short turn-around times? If not, you must decide for yourself whether you really need as fast a service or not.

Many analytical procedures prescribe a maximum allowable storage time for the samples. It is important to be aware of these and to make sure the laboratory respects them. For this reason volatile organics results should be available more rapidly that extractables. The laboratory may choose to send you all the results in a final report, if it isn't suitable to you, it should be possible to receive results as they are being produced.

2.3 The number of significant figures reported.

The number of significant figures reported should reflect the precision of the analysis. The basic premise of the degree of precision of an analytical procedure is the lowest common denominator: the results are only as precise as the least precise measurement during that procedure. For most organic analyses, it is either the volume of the sample, measured in the highly

imprecise graduated cylinder, or the final volume injected, e.g., one µL in a 10 µL syringe. If done manually, the best operators claim 5% error; on the average 10-15 % is probably closer to reality. Modern autosamplers can do better, but the flaw is then usually in the measurement of the volume of the final extract -- 1mL by pipette or syringe.

Therefore, the next time you see on a lab report benzene = 5.245 µg/L, just use this as a mental flag, and raise the question of the number of significant figures with the chemist. Inexperienced analysts have a tendency to report to the client all the digits printed out by integrators without consideration to the meaning of these numbers. If an inordinate number of significant figures are being reported, the instrument output probably received very little review.

2.4 References.

To find a suitable laboratory, like any other professional service, ask other users for their opinion. It is also very acceptable to ask the laboratory to provide a list of their satisfied clients. This doesn't constitute complete assurance, because laboratory performance can fluctuate. Summer is of course a critical period, where the sample load increases, regular staff take their annual leave, and summer students learn how to do their first extraction. This is why QA/QC has to be an ongoing, integrated process for any investigation. For certain critical investigations, it is possible to request that the same group handle all your samples. A well-run analytical laboratory should be able to integrate new personnel without a decline in performance. The user can ensure him/herself of this continued quality by the application of a rigorous quality assurance/quality control program as discussed below (section 3).

2.5 Suggested Reading.

J.K. Taylor (1), in his book " Quality Assurance of Chemical Measurements", devotes an entire chapter to the issue of laboratory selection.

3.0 Selection of analytes

The question of analyte selection in hazardous waste investigations can be very difficult. At some sites, little or no information is available as to the quantities and types of wastes involved, however, as Plumb (2) shows, volatile organic chemicals are frequently present at hazardous waste sites and are relatively inexpensive to measure. If information is available, it often has to be translated into single components. For example, requesting a laboratory to do total coal tar analysis is viewed as impossible. However, most laboratories are able to analyse for the components of coal tar, e.g., benzene, toluene, the

xylenes and the PAHs. This is why, in this section, nomenclature will be discussed before the selection of analytes.

3.1 Nomenclature

Most hydrogeologists have a relatively good background in inorganic chemistry and know which metals and ions are expected to be found in the subsurface. Also, the nomenclature is somewhat more simple because the use of trivial names has been discontinued a long time ago, e.g., hydrochloric acid is now seldom referred to as muriatic acid. Therefore, only the topic of organic chemical nomenclature will be included here.

Organic compounds are those based on carbon. Additional elements in the compounds, in order of abundance are: hydrogen, oxygen, nitrogen and sulfur. There are a multitude of naturally occurring organic compounds, and an equally astounding number of synthetic ones. In synthesis, halogens (F, Cl, Br, I) are most commonly added.

For the hydrogeologist, the name of the chemical is not as important as being able to predict its behaviour in the subsurface. Therefore, the first thing to do when confronted to a new name is to find out its structure, because it contains information that will allow the prediction of its mobility and solubility. Where can this be found? It may be requested from the chemist who reported the data. Alternately, it may be found in a number of handbooks such as the CRC Handbook (3), The Ground Water Chemicals Desk Reference (4), the Merck index (5) or even the Aldrich chemical catalog (6) . The use of CAS numbers* is a good way to ensure that the same compound is referred to.

Compounds that have only C and H atoms are named hydrocarbons. Of all the organic compounds, they are the least soluble in water. They can be saturated or unsaturated, aliphatic or aromatic. Aliphatic compounds are chains or carbon atoms which may be branched or even cyclic. Saturation means that carbon is bonded to four different atoms. Unsaturation means that two adjoining atoms share more than one pair of electrons. If several unsaturated carbons are linked in a cyclic structure where the electrons may be shared over several carbons, the compounds are then aromatic. The term aromatic comes from the fact that certain hydrocarbons do have a pleasant odour, e.g., benzene, toluene, the xylenes and naphthalene fall into this category. All these compounds are cyclic and this special configuration of electrons confers them more stability. The word aromatic should thus be associated with stability.

As other atoms such as oxygen, nitrogen and sulfur are added to the hydrocarbons, their solubility in water increases. Indeed to be solubilized, molecules have to form weak hydrogen bonds with water. The more similar a

compound is to water, the greater is its the solubility. For example, ethanol (CH_3CH_2OH) is more soluble than ethane (CH_3CH_3), and in turn ethylene glycol(or 1,2-dihydroxyethane) (CH_2OHCH_2OH) is more soluble than ethanol.

Often, students claim that they do not understand organic chemical nomenclature. There is nothing to understand in a nomenclature system - it only needs to be learned. One of the problem is the coexistence of several nomenclature systems. This most often arises in biological molecules where the structures are often complex to describe in chemical terms. A good example of this comes from the synthesis of a fungal metabolite called "asperlin" (7) , so named because it is a metabolite of the fungus Aspergillus nidulans. The IUPAC* name for this molecule is: 5-acetoxy- 6(1,2-epoxypropyl)-cis-5,6-dihydro-2-pyrone. But because this molecule was synthetized using the sugar galactose as its precursor, carbohydrate chemists preferred to refer to it as 4-O-acetyl-6,7-anhydro-2,3,8-trideoxy-threo-oct-2-enono-1,5-lactone. This molecule only contains nine carbon atoms! It is not hard to imagine what IUPAC nomenclature would produce for a protein with a molecular weight of 2000.

Since it is easier to learn chemical names and structures if they can be associated with a problem, the wisest learning technique is to look up names and structures as they are met. Groupings them according to structure is also helpful. For instance, polychlorinated biphenyls are a group of biphenyls which only differ in the number of chlorine substituents and thus have similar properties. Polynuclear aromatic hydrocarbons are aromatic compounds which simply differ by the number of fused aromatic rings.

3.2 Target compound analysis vs. the complete analysis.

At the first investigation, the more that can be determined, the better. However, analytical chemistry is expensive and a rational approach is to be recommended. It has been recognized that the analysis for volatiles can be a very relevant cost effective technique for assessing groundwater contamination problems (2,8). The reason is very simple: small molecules are more soluble than their higher molecular weight analog, hence they are more likely to have migrated away from the source. Fully automated purge-and-trap systems are found in the vast majority of North American environmental laboratories and or alternately, headspace analysis can be done rapidly. Portable field gas chromatographs (9) are becoming commonplace in hazardous waste site investigations.

Water miscible compounds, such as acetone, ethanol, acetic acid, 1,4-dioxane and aniline, are a particular problem. Because of their high solubilities, they are very mobile in the subsurface and are the most likely to move off site, but at the

same time the analytical methodologies to address them are often inadequate (10).

Volatiles should therefore be screened in the first analysis, but a more complete analysis should be done closer to the source. Quantitative analysis of U.S. EPA Appendix IX compounds should be mandatory for selected samples, but it should be remembered that no single list is comprehensive, and that most analytical methods are selective. Also, a good proportion of the chemicals found in a typical hazardous site are not on any priority list. There are major difficulties inherent to their measurement as will be discussed by Swallow (11) Metal ions should not be neglected as well as basic field measurements, e.g., pH, Eh and dissolved oxygen.

4. QA/QC

The term quality assurance/ quality control finds its way in most analytical contracts, yet a little probing showed that it meant different things to different people. The often heard phrase: "We sent duplicate samples to another lab and their results are different than yours, why?" summarizes the frequent failure of what is assumed to be QA/QC by many inexperienced investigators. At that point, there is very little that can be done to salvage the data. The best approach is to design the QA/QC program before the first sample is taken.

4.1 Definition

The importance of quality assurance/quality control program is being increasingly recognised primarily through the efforts of the US EPA (12) which laid out precise guidelines for the implementation of QA/QC for the validation of analytical data.

Unfortunately, this has not made its way into the curriculum of most university analytical chemistry courses, thus, even the meaning of the words is subject to different interpretation. Regardless of how one wants to label them, QA/QC programs need to be operated at two levels. Firstly, within the laboratory, to ensure that good laboratory practice is consistently utilised and that the results achieved are of consistent and measurable quality, i.e., quality control. This means that, for example, the chemist reporting the results needs to ensure that a concentration of 5.2 µg/L of benzene is accurate (i.e., it wasn't in fact 2 or 10) and that the degree of precision of this measurement (i.e. 5.2±0.2 or 5±1 µg/L) and the detection limit for the sample analysed can be given to the client. Secondly, external control by the client has to be implemented to ensure comparability of data obtained from different sources and over different time periods. In other words quality assurance is what the client needs to do to

ensure the reliability of the results of the analyses. The sections below will describe how this can be achieved.

4.2 Precision and Accuracy.

Precision is the degree to which data generated from replicate or repetitive measurements differ from one another (13). It is obtained by the repetitive analyses of standards, for the method precision, and of samples, to assess the degree of variation between replicates. Any reputable commercial laboratory will provide data on the precision of their analytical methods, but it is the responsibility of the client to request the appropriate number of replicates.

Accuracy is the degree of agreement of a measured value with the true or expected value of the quantity of concern (1). It is more difficult to assess than precision, but can be evaluated by analysing certified reference materials and participating in inter-laboratory comparisons, also known as round-robins*. Certified reference material are not available for many analytes and matrices and interlaboratory studies are infrequent. It is possible to get a measure of accuracy by having another laboratory send some spiked samples mixed with the batch of samples submitted.

Therefore what are the practical tools to ensure that the quality of data obtained meets expectations? Split samples? As stated above, the two main factors that need to be assessed are precision and accuracy: split samples will do neither. If the two data sets agree, it may be fortuitous. If they do not agree, it will not be possible to measure of whether this falls within normal analytical error and to know which value is the accurate one. The only answer is to prepare a QA/QC progam which suits the size and schedule of the sampling program.

4.3 QA/QC Programs.

For large field projects, the regulatory agency will often dictate the QA/QC program. However, for smaller investigations or in countries other than the U.S.A., this task is typically the responsibility of the investigator. An example of an adequate QA/QC program is outlined in Table 1. The total number of QA/QC samples need to be approximately 10-15% of the total sample load, relatively more if the batch size is small. This includes blanks*, replicates* and spiked* samples. Blanks should be reported and it is important to find out whether or not the data was corrected for blanks. Replicates are important because they will be the only measure of sample variability. For this reason, it is preferable to do one sample in triplicate rather than two samples in duplicate. The cost will be the same, but statistical evaluation cannot be done on duplicates. In the example given in Table 1, only three samples were quality assurance samples, the field blank and two of the three replicates. This

should be sufficient in a batch of 12 samples. The laboratory inserted reagent blanks after the standards and after a series of samples to find out about possible carryover. The standards were measured at two different concentration levels to allow the construction of a standard response curve (the blank is used for the third data point). This does not always happen in organic analysis because if fifty or more analytes are measured simultaneously, the calculations may be somewhat cumbersome.

Table 1. Example of a laboratory load with very good quality control

Run #	ANALYSIS
1.	Standard concentration level 1
2.	Standard concentration level 2
3.	Blank (reagent grade water)
4.	Sample 1
5.	Sample 2
6.	Sample 3
7.	Sample 4
8.	Sample 5 replicate
9.	Sample 5 replicate
10.	Sample 5 replicate
11.	Blank (field or travel)
12.	Standard concentration level 1
13.	Standard concentration level 2
14.	Sample 6
15.	Sample 7
16.	Sample 8
17.	Sample 9
18.	Sample 10
19.	Sample 11
20.	Sample 12
21.	Blank (reagent)
22.	Standard concentration level 1
23.	Standard concentration level 2

NOTE: Surrogates are added to all samples

Spiked samples are used to measure matrix effects and possible bias on the data. This is most important in hazardous wastes samples because many of the contaminants may be present in high enough concentration to act as cosolvents and change the composition of the extracting solvent. Indeed an analytical method developed for water may not be suitable for a concentrated landfill leachate. Unfortunately, unless the expected concentration of the analyte is known ahead of time, it is very difficult for the laboratory to spike the sample at a realistic level.

The matrix effect is measured by comparing the percentage recovery of the spiked compound in the sample compared to what has been found in distilled water. The percentage recovery of the analyte is calculated as follows:

$$Recovery\ (\%) = \frac{(Amount_{spsamp} - Amount_{ussamp})}{Amount_{sp}} \times 100$$

where
spsamp = spiked sample
ussamp = unspiked sample
sp = spiked

In highly contaminated samples where the analytical error is large, it is not unusual to find more in the unspiked sample than in the spiked sample and hence get a negative recovery, e.g.,

$$Recovery = \frac{624 \pm 230\ \mu g - 750 \pm 250\ \mu g}{100\ \mu g} \times 100$$

The large standard deviation will often be due to the fact that the sample had to be diluted to stay within the capacity of the chromatographic column and hence is 23 x 10, because of the dilution factor. Thirty percent standard deviation is not at all rare for organic analysis. Had the sample not had to be diluted, 100 µg would have been a very realistic spiking range. Unfortunately, only after the sample has been analysed once is it possible to gauge the appropriate dilution range.

Because the same amount of information can be gathered with one analysis

instead of two, and because they are not likely to be found in the samples, spiked samples have been largely replaced by surrogates.

4.4 Surrogates and Internal Standards

A surrogate is a compound which is an analog of the analytes and is added to the sample prior to the extraction step. It can be a deuterated (where deuterium has replaced hydrogen) analog most commonly used in GC-MS, or a chemical analog which would not be expected in the samples. It is carried through the whole analytical procedure, and its recovery is reported as a measure of matrix effect and analytical error. The ultimate would be to have a deuterated analog for each analyte (isotope dilution) as described in EPA method 1624 and 1625 (12) but the costs involved preclude its widespread usage.

Surrogates are not to be confused with internal standards. Internal standards are also usually deuterated analogs, but they are added in the final analytical step and are used for quantitative analysis where their purpose is to account for instrument variability from one sample to the next. The area of the peak of the internal standard in the sample run is compared to the area of the internal standard in the standardization run and all the concentrations are corrected for any discrepancy.

$$Concentration\ of\ x = \frac{Area\ x_{samp}}{Area\ x_{std}} X \frac{Areal.S._{std}}{Areal.S._{samp}} X\ Conc\ x_{std}$$

where
x = analyte (or parameter)
samp. = sample
std = standardization run
I.S. = internal standard

It is possible to use more than one internal standard in an analysis to account for the possible behaviour of either early or late eluting compounds, or of acidic and neutral compounds. During purge and trap analysis for volatiles, surrogates and internal standards are added together since there is no other preliminary extraction step. Then, the only difference between the two is that internal standards are used in the calculations whereas surrogate concentrations are simply reported.

In a typical laboratory report, the percentage recovery for surrogates is reported for every sample. Obviously 100% is the target, but acceptable recoveries ranges are much wider as shown in Table 2.

Table 2 . Surrogate spike recovery limits for water and sediment samples for neutral, acidic and volatile compounds (14).

Surrogate	Water	Sediment
Nitrobenzene-d5	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
p-Terphenyl-d14	33-141	18-137
Phenol-d6	10-94	24-113
2-Fluorophenol	21-100	25-121
2,4,6-Tribromophenol	10-123	19-122
4-Bromofluorobenzene	86-115	74-121
Dibromofluoromethane	86-118	80-120
Toluene-d8	88-110	81-117

5. GC-MS ANALYSIS.

At the vast majority of hazardous wastes sites, organic chemical analysis is conducted by coupled gas chromatography-mass spectrometry. This is primarily because while it is relatively expensive, it is the most cost effective analysis if the amount of information obtained per analytical dollar spent is considered. This section will cover the basic principle of GC-MS analysis and its use as both a qualitative and quantitative analytical instrument. Other mass spectrometric techniques will be described briefly. The emphasis will be placed on the quadrupole instruments since they are currently the most popular in environmental analysis.

5.1 Trace organic analysis

The principle behind most organic analysis is the same and is illustrated in Figure 1. Compounds dissolved in water are extracted (by a gas for volatiles or a solvent for semi-volatiles) and separated by chromatography. Their presence is detected by a detector, the output of which will be proportional to the total amount of each component. Quantitation of components is done by integrating the area under the chromatographic peak and comparing it to that of

a standard. The specificity of the analysis depends on the type of detector used. It may be relatively non-selective such as the flame ionization detector (FID) where essentially anything that will burn is detected, to a fairly specific one, such as the electron capture detector (ECD) which will almost only detect halogenated compounds. If a mass spectrometer is used as a detector, it can be used as both a non-selective and a specific detector.

5.2 Basic principle

A mass spectrometer is an instrument which differentiates compounds according to their mass. It is composed of three main parts: the ionization chamber, a mass filter (magnetic field or electronic mass filter) and a signal amplifier (electron multiplier). The compound enters the ionization chamber and is bombarded by a current of electrons at 70 eV in a vacuum. This causes the molecule to loses an electron and acquire a positive charge (z). The charged molecule is then destabilized and tends to break down into several smaller fragments along its weakests bonds. These ionic fragments will be attracted to the detector which is of the opposite charge. In a quadrupole instrument the ionized particles will travel through a set of four rods (2 neg and 2 pos) to which DC voltages are applied and act as an electrostatic filter. The ratio mass/z transmitted is proportional to the amplitude of the applied rf, which is scanned with time to allow a selected range of ionized molecules to reach the elecron multiplier. For a more detailed discussion, the readers are referred to a publication by Haas and Norwood (16). The mass/z ratio is representative of the molecular mass of the compounds and is thus usually referred to in atomic mass units (a.m.u. or daltons).

5.3 Data acquisition

GC-MS analyses can be done in two main modes, full scan or selected ion monitoring. In the first mode, a range of masses (typically 45 to 450 a.m.u.) are acquired at the rate of one scan per second, that is every second a full mass spectrum is obtained and stored in the computer for later retrieval (Figure 2). The word "scan" refer to scanning of the rf voltages as noted above in a range proportional to the selected masses. In the selected ion mode, only a group of ions, which are typical fragments of the analytes of concern, are acquired (Figure 3). The scan will only contain the intensity of these ions. Because usually a maximum of 10-15 ions are monitored simultaneously, the scan rate, i.e. the number of scans per second, can be increased resulting in an increase in sensitivity. Because only a few masses are acquired it is not possible to identify unknowns in the sample. Also, in heavily contaminated samples,

interferences can cause problems. If a large quantity of analytes are requested, the gains in sensitivity are relatively small and thus it is preferable to acquire using a full scan.

Even when a full spectrum is acquired, quantitative analysis is done on extracted ions (Figure 4). One ion is selected for each compound for quantitation. Each ion is in essence a specific detector. As in any chromatographic analysis, the area under the curve of a specific time window is integrated, then the area of the unknown is compared to that of the standard. In addition the area of one or two other ions characteristic of the analyte are also integrated and their ratio compared to that of the primary ion; these are termed qualifying ions because they allow for qualitative identification of a compound. Under the same operating conditions, the spectrum obtained from a given compound is always the same, hence the ratios of the qualifying ions to the primary ion are constant and in addition to the retention time are the criteria that are used to ensure the correct identification of the analytes (Figure 5).

The strength of GC-MS over conventional GC detectors is therefore twofold. Quantitation using a selected mass which is characteristic of the target analyte ensures selectivity and reduces the problem of coeluting interferences. For example, if two peaks were to elute closely, but one is from benzene (mass 78) and the other one for carbon tetrachloride (mass 117), an unspecific detector would see the summed response from the two compounds in the overlapping region. With the mass spectrometer a different chromatogram can be drawn for the two masses where interference from the coeluting compound is totally eliminated (Figure 3). The acquisition of a complete mass spectrum allows for the unambiguous identification of the correct analyte peak and allows for the tentative identification of peaks arising from non-target analytes.

5.4 Library searches

The identification of the components in a mixture is done by comparing the spectrum of the unknown to that of a library of spectra stored in the GC-MS computer. There are two main methods of doing this comparison, forward search and reverse search (Table 3) .

During a forward search, the spectrum of the unknown is compared to that of those contained in a library, either commercially available, such as the NBS library of spectra which now contains the spectrum of over 42,000 compounds, or a user created library which, although usually more modest in size, can be tailored to specific types of compounds and be more efficient. For instance, a pharmaceutical company may wish to use a library containing drugs only. In groundwater analysis, the broader library is the most useful since the

contaminants may originate from very diverse sources such as agricultural runoff, industrial spills and landfill leachates. The output from the search consists of a list of best matches ranked in order of best fit. A perfect match would carry a fit index of 100; this is seldom observed, although matches of 90-95 % are not uncommon. When the match is of lesser quality, the chemist must interpret the differences and make a tentative identification. Often the spectrum of the unknown is not present in the library and at best the library search will give an indication of the chemical class of the compound. The mass spectrometer is not very effective in distinguishing between different isomers, because they usually have very similar spectra. Thus, if a series of dimethyl naphthalenes are present in a sample from a wood-preservative site, identification of the correct isomers can only be done by comparing with standards.

In a reverse search, a group of spectra contained in a user-created library are compared to all the spectra found in a sample. This type of routine is used in target compound analysis. The advantage of this type of search is to be able to identify much lower quantities of a compound than is possible in a forward search because, even if the peak is of very low intensity or is buried in a group of poorly resolved peaks, it will still be found. This is the type of search that is used in priority pollutant analysis by most laboratories. The danger of restricting oneself to this type of analysis is to miss some non-target compounds that may be very important. Therefore, whenever a "GC-MS scan" is requested from a laboratory, it is essential to clarify whether a forward search will also be carried out to identify "what else may be there". Because forward searches are much more time consuming, the cost is likely to be higher, but it is the only way to ensure that important constituents are not overlooked.

Table 3. Forward Search vs. Reverses Search .

FORWARD SEARCH
- THE SPECTRUM OF AN UNKNOWN IS RECORDED
- IT IS COMPARED TO A LIBRARY OF SPECTRA
- A TENTATIVE IDENTIFICATION IS MADE

THIS IS THE ONLY OPTION AVAILABLE WHEN NO STANDARDS ARE AVAILABLE

REVERSE SEARCH

- A STANDARD IS ANALYSED
- A RETENTION TIME WINDOW AND A SPECTRUM ARE OBTAINED
- MASSES CHARACTERISTIC OF THE COMPOUND WILL BE SEARCHED IN THE SAME RETENTION WINDOW

THIS IS THE TECHNIQUE USED FOR QUANTITATIVE TARGET COMPOUND ANALYSIS.
- ONLY POSSIBLE IF A STANDARD IS AVAILABLE
- ALLOWS FOR MUCH LOWER DETECTION LIMIT EVEN IN COMPLEX SAMPLES

5.5 Problem samples.

Analytical methods are validated for a given analyte or group of analytes in a specific matrix (e.g. water, soil, sludge etc...) and for a determined concentration range. When the concentration in the samples fall outside of this range, it becomes necessary to either increase the sample size if the analyte is too dilute, or to decrease the sample size when the sample is too heavily contaminated. Either way, this affects the precision and accuracy of the method and should be taken into consideration when evaluating the data. At many hazardous waste sites, the concentration of one or more analyte often exceeds

the working range of methods designed for relatively clean water and soils, therefore requiring sample dilution.

The major effect is, of course, to correspondingly reduce the detection limit of all the analytes present in the samples. Minor constituents will therefore be lost. It is sometimes possible to analyse the sample at two different dilutions, but this will only be effective if the high concentration contaminants elute relatively far from the lower concentration analytes (i.e., are well separated on the chromatograms). The potential for contamination of the analytical instrument makes this approach impractical. For semi-volatile compounds, a liquid chromatographic cleanup can be done on the extract. This fractionates the sample according to chemical classes, and is only useful in target compound analysis. For volatiles, no such scheme is possible, because most of the analytes would be lost during processing. It is thus customary to simply dilute the sample with "organic free" water. Unfortunately, it is virtually impossible to obtain totally organic free water. Also the polymers used in the traps of the purge and trap system are also organic and can bleed small quantities of compounds such as benzene and toluene.

This problem can be corrected by analysing appropriate blanks, but, since there is always a slight variation between analytical runs, there is often a residual amount carried over, usually close to detection limit. When a sample has been diluted 100 fold, a residual of 0.3 ug/L of benzene will become a reported concentration of 30 ug/L, which may seem significant. When evaluating data arising from diluted samples, it is important to remember to readjust the detection limit and the associated analytical error accordingly. In this case, the detection limit would be 10 µg/L (not 0.1 µg/L). To reflect the actual accuracy of the data, it would be best reported as 0.03 mg/L with a detection limit of 0.01 mg/L. Unfortunately not all analytical laboratories follow this policy and the client has to exercise his own judment in evaluating the data.

6.0 Other Organic Analytical methods.

As discussed above, GC-MS analysis has a lot to offer because it can provide qualitative and quantitative analysis as well as confirmation of the identity of compounds. It does however have limitations. Only compounds that are sufficiently volatile, or which can be made volatile through chemical derivatization, are amenable to GC-MS analysis. For semi- volatile compounds, an extraction is ususally done in dichloromethane prior to introducing the sample into the instrument, thus, only extractable compounds are suitable for GC-MS analysis. In environmental samples, this can be as little as 10-15% of the total dissolved organic carbon.

Also, some samples are sufficently unstable to warrant immediate on-site analysis. At the moment there are very few portable GC-MS systems that can be brought to the field. Some mobile laboratories have been equipped with mass spectrometers (the Ontario Ministry of the Environment has small vans equipped with TAGA* systems, a product of Sciex instruments, Mississauga, Ontario, Canada) but in general they are restricted to air sampling where no sample preparation is necessary. Portable gas chromatographs (9) are invaluable tools for field monitoring. Analysis either on-site or close to the site has definite advantages in hazardous waste sites investigations and at the moment this need is best filled with GCs and HPLCs.

6.1 Gas chromatography

Gas chromatographs with specific detectors can outperform GC-MS systems in terms of specificity and detection limit. The electron capture detector was for a long time the sole instrument used by pesticide chemists and is still routinely utilised for chlorinated pesticides and PCBs. One of its advantages is its specificity for certain group of compounds, mostly halogenated hydrocarbons and nitro-substituted compounds. It is also at least one hundred times more sensitive than mass spectrometers, even in the selected ion mode. Furthermore, it is much less expensive and thus is a very cost effective means of analysis. Other commonly used detectors include the flame ionization (FID), a good multipurpose detector often used in hydrocarbon analysis; the thermal conductivity detector (TC), used in gas analysis at the percentage level; the photoionization detector (PID), used mostly for aromatic hydrocarbons, but also in portable GC's such as the Photovac (Thornhill, Ontario); the nitrogen/phosphorus detector, also called the alkali flame detector, which is used for nitrogen and phosphorus containing pesticides.

6.2 High Pressure Liquid Chromatography (HPLC*).

HPLC is the analytical tool of choice for most thermally labile* compounds. In HPLC, the carrier gas of the GC is replaced by a solvent mixture, most of the time containing a large proportion of water. It is thus quite logical that, where the sample matrix* is water, HPLC could be the instrument of choice. Several detectors have been developped for the liquid chromatographs, the most popular being the ultraviolet, the fluorescence and to a lesser extent the electroconductivity detectors. Ion chromatographs are in essence liquid chromatographs with conductivity detectors. There are two main reasons why HPLC is not used for all analyses: (a) the efficiency of the separation is not as good as what can be achieved with a capillary gas chromatograph and (b) the detection systems are not as sensitive, except for the fluorescence detector, but then, not all molecules fluoresce or can be derivatized to fluorescent species. The derivatization reaction can be carried out post-column, i.e., following

sample elution from the chromatography column. A good example of this in ground-water contamination is the analysis for the pesticide aldicarb and its two toxic metabolites, aldicarb sulfone and sulfoxide (17). The three compounds are separated on the HPLC column, then hydrolysed and derivatized to the same fluorescent species.

Diode array detectors are used in HPLC analysis instead of U.V. detectors. They are scanning U.V. detectors and can provide confirmatory data for HPLC analysis in the same way the mass spectrometer does for the gas chromatograph. However, a U.V. spectrum is not nearly as useful as a mass spectrum in the identification of organic compounds because it is not as detailed, however, there are situations where it is the only possible choice. An example of this is the case of a hazardous waste site where the presence of both phenol and aniline was suspected (18). These two compounds elute very closely in a gas chromatograph. Phenol has a molecular weight (M) of 94, and aniline of 93. However, because carbon has both C-12 and C-13 isotopes, there is always a significant M+1 peak in a mass spectrum in organic compounds. Therefore aniline also has a peak at 94. The fragment ions are also similar, which means that mass spectrometry is useless in telling them apart. Aniline also interferes with the total phenols measurement by the 4-amino-antipyrene colorimetric test. The two compounds also elute closely in HPLC, but their U.V. spectra are sufficiently different that it is possible to distinguish them by diode array detection (Figure 6)

6.3 Other Hyphenated Methods

There are also LC-MS instruments on the market, but they are not nearly as widespread as GC-MS system, partly because they are much more recent. Indeed interfacing an LC with a MS is a much more difficult task than coupling a GC to an MS. The MS needs to operate in a vacuum, whereas the effluent of an LC is a solvent, mostly water, mixed with buffer salts. Many ingenious interfaces have been devised, but there is invariably a trade-off in terms of sensitivity (19).

There are several other hyphenated instrumental method of analysis now available on the market. Most of these are not accepted in regulatory methods because they are either too scarce or still considered too experimental. One of these promising tools is th GC-FT-IR (20, 21). This instrument which gathers infra-red spectra instead of mass-spectra, is an excellent complementary tool to GC-MS. It addresses the same range of compounds, but the spectrum obtained gives information on the functional groups of the molecule. For instance with IR, it is very easy to distinguish alcohols from ketones and esters. It is also

possible to distinguish between isomers, e.g. between ortho, meta and para-xylenes.

GC-MS-MS systems are used to distinguish between very similar compounds by allowing the analyst to get the mass spectrum of one spectral peak of the first mass spectrum. These instruments contain three quadrupoles in series, operating as magnetic/electrostatic/magnetic fields (B/E/B configuration). The molecule in the ion source fragments along its most vulnerable bonds first, and these are separated by the first quadrupole. The second quadrupole acts as a second ionization chamber and further fragments the molecule. These fragments, also called daughter-ion are then separated by the third quadrupole and detected as in the simple MS. This is useful in the case where similar molecules have initial fragments of the same mass/charge ratio. However when these initial fragments are isolated and bombarded a second time, the secondary fragments will differentiate them. The first mass spectrometer can be tuned to allow compounds of only a certain molecular weight to reach the second mass spectrometer. In effect, it acts as an electronic cleanup system.

7.0 Sampling and Field Methods

The sampling of contaminated ground waters requires a careful choice of monitoring instruments. The principal criterion of choice being that the individual hydrostratigraphic units within a ground-water flow system must be sampled individually. Wells that penetrate more than a single unit provide little useful information (22, 23). This is because the sample mixing and dilution that occurs in a fully penetrating well imply a greater hydrodynamic dispersion than actually takes place in the aquifer itself. It is also because this integrated (and diluted) sample may indicate contaminant concentrations within the acceptable limits of the guidelines, although these limits may in fact be exceeded within a particular hydrostratigraphic unit.

Figure 7 shows two commonly used devices for sampling ground-water quality: the bundle-type multilevel and the 2" or 5 cm i.d. piezometer. Both provide the capability of sampling small zones of potentially contaminated ground water. The first is used to map the outlines of contaminant plumes in three dimensional details (24). The second is generally used for monitoring ground-water quality where it is necessary to detect ground-water contamination or to establish that this quality is in compliance with regulated or guideline values. Consequently, the screen material is made of an essentially inert material (e.g., stainless steel). Cowgill (25) presents evidence that the well casing materials

and sampling devices, except those made of PTFE (Teflon), should be steam cleaned prior to use or installation respectively.

Samples for detection or compliance monitoring are best collected using dedicated submersible pumps with PTFE bladders operated by compressed air or nitrogen that does not come into contact with the ground-water sample (26). The pumps (see Figure 7) are located at the depth of the well screen and can be isolated from the stagnant water in the well bore by inflating a packer system, located immediately above the pump. Generally, two or three well screen volumes of stagnant water are pumped before sampling begins (27,28).

Figure 8 shows the sequence of operations conducted inthe field to collect samples and the subsequent distribution of aliquots for analytical purposes. Samples are collected in precleaned (and baked) amber glass bottles, with no headspace for volatile organic samples, at a pump delivery rate of 100 mL/min or less. The bottles are allowed to overflow by at least 1.5 volume then rapidly capped and stored at about 4°C until analysed (29). Sample bottles should not be rinsed out with the sample because a film of organic compounds from any non-aqueous phase liquids present may adhere to the glass and artificially increase the concentration in the sample.

Measurements of certain unstable constituents, e.g., pH, Eh, temperature (T), and specific electrical conductance (SEC), must be conducted in the field. Although referred to as "well purging parameters" (29), in that they are monitored during purging operations and stable readings indicate the appropriate time for sampling, these parameters are critical in the quantitative assessment of water quality (30). Baedecker and Cozzarelli (31) discuss the collection of ground waters for dissolved gas analyses, in particular O_2, H_2S, CH_4, NH_3 and CO_2 (i.e., alkalinity), which are critical in understanding the nature of redox processes within the subsurface.

Preservation techniques for organic constituents of ground water differ from those for inorganics. In particular, it is inadvisable to subject samples collected for volatile organic analysis to vacuum filtration because of the potential losses by volatilization. However, samples for the analysis of volatile aromatic hydrocarbons (e.g. benzene, toluene, ethyl benzene and xylenes - BTEX) should be preserved with HCl to prevent biodegradation (12). Inorganic cations are usually filtered and acidified to pH<2 to prevent precipitation or sorption to the container walls, while samples for inorganic anions are usually only filtered and refrigerated. Kent and Payne (32) show the importance of the filtration of suspended solids in inorganic analysis and present evidence that blue ice packs do not adequately chill water samples to 4°C unless the samples are prechilled with wet ice.

Apart from precision and accuracy (see section 4.2), ground water samples must also be representative of the hydrostratigraphic formation from which they were collected, complete in the sense that the ground-water flow system at the site in question has been fully examined and, finally, comparable with other data collected from the same site. These five attributes define the quality of environmental data and are known as the PARCC attributes (33). The latter three attributes are more the responsibility of the hydrogeologist than the analytical chemist, who is responsible for proper precision and accuracy. Good examples of hydrogeochemical studies of hazardous waste sites that observe the PARCC requirements are those of Barcelona et al. (32? 1989), Jackson and Patterson (30) and several of the chapters in this book.

7.0 Case study: Newcastle, New Brunswick, Canada.

7.1 The problem

This example taken from the report of a review team composed of hydrogeologists and chemists from WMS Associates, Intera Technologies and the National Water Research Institute of Canada (34), was chosen for several reasons. It illustrates clearly the need for strict quality control; it is a good example of how to choose the correct target analytes; and it demonstrates the necessity for hydrogeologists to establish good communication with the analytical laboratory and to include the chemist's viewpoint in the overall assessment of the problem.

The town of Newcastle's (population 7,000) drinking water supply is derived from pumping wells which draw water from a buried-channel sand and gravel aquifer underlying the town. A wood preservation plant that had utilised PCP and creosote for 50-60 years is situated on the outskirts of the town. This plant has been regarded as a potential threat to the municipal water supply and the plant site is scheduled for cleanup. In the interim, the Provincial Government has been monitoring the water supply wells for the presence of PAHs, compounds known to be present in creosote and feared because of their toxicity. In 1988, low levels of PAHs (< 1 µg/L total) were reported present in certain wells at certain times. During 1988 and 1989, PAHs were found intermittently during detection monitoring and both wells were closed in early 1989 due to the exceedence of the 10 ng/L ppt) World Health Organization drinking water limit for benzoa)pyrene. The source of PAH contamination had not been definitively identified, although both the Provincial Government and the community suspected the wood preservation plant.

Examination of the chemical analysis data revealed a number of QA/QC and other problems:

- the lack of a proper protocol for the sampling and analysis of compounds at or near detection limit or the WHO guideline value of 10 ppt;

- no field blanks had been taken to assess the possibility of other sources such as diesel fumes in the pump house or cigarette smoke and no replicate sample had been analysed to measure the precision of data;

- the occurrence of the PAHs was sporadic, with different compounds being identified during different sampling rounds and more soluble, more mobile compounds present in creosote were not detected together with the PAHs;

- the chemist who had reported the data suggestying low-level PAH contamination of the wells had expressed some concerns over the validity of his data at the low level of detection requested by the regulators and admitted having had very little experience doing this type of analysis; and

- the water supply wells used for detection monitoring did not appear to be suitable as monitoring wells with which to establish the level of contamination of the aquifer.

7.2 The plan.

A complete study was therefore commissioned to find out whether the aquifer was indeed contaminated with PAHs and if so, what was the source of the contamination. A survey of the area was conducted to determine all the possible sources of PAHs. Apart from the plant mentioned above, there were several possiblities: a dumpsite, a small lumber company using wood preservatives and several potentially leaking fuel storage tanks.

A new set of monitoring wells were drilled with a cable-tool rig i.e., one needing no compressor or other component producing PAHs) using a rigorous cleaning protocol for the drilling equipment to prevent contamination with any oil or grease. The steel casing was washed with degreasing solvent, detergent, a hot water rinse, acetone and finally a distilled water rinse prior to use. Samples of the rinse waters were collected and analysed. Each monitoring well was installed with a dedicated submersible pump to prevent cross-contamination between wells.

Three rounds of sampling were done. The QA/QC program included equipment rinse samples, drill water samples, trip blanks, field blanks and replicates. The samples were also sent to two laboratories: the one that had published the initial results and a commercial laboratory which was deemed reliable by the review team.

The list of selected analytes was expanded to include, in addition to the PAHs, the volatile organic compounds benzene, toluene and xylene as well as EPA priority pollutant phenols in order to assess the source of the contaminants. As explained above, the more mobile compounds are the most soluble ones. It was known from studies done by Goerlitz at the USGS (35) that water contaminated by wood preservatives would indeed contain PAHs, and that naphthalene would be the predominant species; phenols, mostly methyl and dimethyl phenols would also likely be found. From other work (36) it was known that the volatiles benzene, toluene and xylenes should be also present since they are a component of creosote and are even more soluble than naphthalene. Nitrogen containing heterocyclic compounds should also have been used, but it was impossible to find a commercial laboratory that was immediately able to carry out this analysis quantitatively. Because the city water supply was shut down, bottled water was being used at great expense and inconvenience and the replacement aquifer supply was still under development, it was important to carry out this project as diligently as possible.

7.3 The results.

Equipment rinse samples were generally found to contain low levels of phenols and occasionally some PAHs. Drill water samples showed trace levels of phenol < 0.2 µg/L) and cresol, but no PAHs. Distilled water exposed to diesel engine exhaust fumes resulted in low levels of fluorene and phenanthrene 0.17 and 0.29 µg/L resxpectively). No PAH were detected in the water exposed to a gasoline engine exhaust or to cigarette smoke.

PAHs were found in two of the three sampling rounds, but the results of the two laboratories did not corroborate with each other. One of the labs found phenanthrene, fluorene and fluoranthene, whereas the other one only found naphthalene. As with all split samples, this did not tell the reviewing team anything other than the two labs did not agree. Both labs were requested to participate in a round-robin specifically designed to test for the analysis of low levels of PAHs in water, the results of which could be used to assess their capabilities and weaknesses. The next step was to question both laboratories about their procedures to try to explain these discrepancies.

Laboratory #1 did admit to having blank problems at the low level. A close look at their raw data and their procedure showed that although naphthalene was listed on their report sheet, their procedure did not measure it. For them, somehow, not detected and not reported was equivalent. Their internal quality control was insufficient, as they did not add any surrogates to their samples, the precision of their results could therefore not be assessed. Laboratory #2 used naphthalene-d8 as a surrogate and were reporting constant recoveries for all their samples. They also had a measurable naphthalene concentration in their laboratory blanks. The naphthalene concentration reported for the samples were three times as high. When questioned as to whether they regarded this as significant or not, they replied affirmatively. Upon further insistance by the review team, they explained that somehow they had not been told in advance that they were expected to do PAHs and phenols and they had to carry this analysis on 300 mLs instead of the usual liter. In the review team's opinion, the naphthalene found in the blank was most likely to be from an impure deuterated surrogate standard. Because the sample size was a third of the normal, this number was multiplied by the dilution factor, i.e. 3, which accounted for the apparently significant naphthalene concentration. The dilution factor should have been noted on the laboratory report, but it wasn't.

Was this sufficient evidence to say that the earlier reports were false positives? Probably, but moreover, no phenols or volatiles were detected in any of the samples. Without the presence of such mobile contaminants in the monitoring well network, the review team suspected that the reported occurrences of PAHs "hits") were simply false positives.

7.4 Conclusion.

This very expensive exercise costing several million dollars could have been avoided if the initial sampling had been conducted with proper quality control. The choice of target parameters which are complementary is very important, as no single piece of evidence, even if it is done by GC-MS, is sufficient to conclude with certainty. Maintaining a very close dialogue with the analyst and the sampling team is very important for the hydrogeologist, in order for her or him to know how the samples were effectively collected shipped and analysed.

GLOSSARY

A.m.u.: atomic mass units or daltons; the mass of a compound calculated from its formula using the lowest isotopes expressed in daltons is not to be confused with its molecular weight which takes isotope abundances into account.

Accuracy: the amount of bias that a sample may be exposed to during sampling and laboratory analysis (33). the degree of agreement of a measured value with the true value or expected value of the quantity of concern (1).

Blanks: samples of the matrix only, used to evaluate possible sources of contamination during sampling and analysis.

Blind sample: a sample, spiked with known amount of a standard solution, sent to the laboratory within a batch of samples. It will help to detect any bias, or systematic error of the laboratory. However, they are usually very easily spotted by the laboratory because of their unusual mixtures. The same results may be obtained by sending a set of standards, they need not be blind.

CAS number : in an ultimate attempt to solve the nomenclature problem, the Chemical Abstract Service has come up with a numbering system based on structure. It is an excellent idea to double check the CAS number to ensure that the same chemical is being referred to. One drawback is that very few people can construct a structure from the number. However, they are easily retrieved from a computer.

Comparability: the ability to fairly compare sample test results taken from the same facility at different times (33).

Completeness: the number of samples that must be taken and analysed before a confident judgement can be made that the ground-water conditions at a facility have adequately been assessed (33). A measure of the amount of data obtained from a measurement process compared to the amount that was expected to be obtained under the conditions of measurement (1).

Field blank: A sample of purified water that is transferred to a sample bottle at the same time as the samples are collected. Its' purpose is to ensure that air contaminants are not introduced in the samples at the site. Fuel fumes from pumps and gasoline generators are a common source of problems.

GC-FT-IR: Gas Chromatography coupled to Fourier Transformed Infra-Red spectrometry. Spectra obtained in the Fourier domain can be easily accumulated, hence this is a method of enhancing the signal from the infra-red spectrometer. When coupled to a GC, the system can be used in much the same fashion as the GC-MS is, with comparison of unknowns with a standardized library of spectra. Infra-red spectra allow for the identification of types of functional groups in a molecule alcohols, amines, ketones etc..) as well as allowing to distinguish between positional isomers such as o- and m-xylene).

GC-MS: Gas chromatography coupled to mass spectrometry. The gas chromatograph separates mixtures in the gas phase into their components. The mass spectrometer detects them and allows for their quantitation and identification.

HPLC: High Pressure Liquid Chromatograph. This instruments separates mixtures of compounds dissolved in liquids. It is mostly used for aqueous samples and for thermally unstable compounds.

Isomers: Compounds which have the same molecular formula molecular weight as well of course) but where the functional groups or atoms are arranged differently and hence have a different structure.

IUPAC: International Union of Pure and Applied Chemistry. This organization has proposed a standardized system of nomenclature.

Matrix: The material in which the analyte is dissolved; water, soil, effluents, landfill leachates and sludges are typical matrices in environmental analysis.

PAH: Polynuclear Aromatic Hydrocarbons-a group of compounds commonly found in fossil fuels- some of which have been found to be carcinogenic. The smallest of the group is naphthalene, used in crystal form as mothballs. Benzo-a-pyrene is ususally the regulated one, whith a drinking water limit of 10 ng/L World Health Organisation).

PNA: PolyNuclear Aromatics - an alternate name for PAHs.

PCP: Pentachlorophenol. Compound used as a pesticide, mostly as a wood-preservative.

Precision: The average amount of variability experienced in collecting and analysing a sample, expressed as the relative standard deviation (33). The degree to which data generated from replicate or repetitive measurement differ from one another (13).

QA/QC: Quality assurance/quality control.

Quality assurance: a system of activities whose purpose is to provide to the producer or user of a product or a service the assurance that it meets defined standards of quality with a stated level of confidence (1).

Quality control: the overall system of activities whose purpose is to control the quality of a product or a service so that it meets the needs of the users. The aim is to provide quality that is satisfactory, adequate, dependable and economic. (1).

Replicates: in an experiment repeats using the same variables. In analysis, repeats of the same sample using the same analytical conditions.

Representativeness: a subjective assessment of whether the sample truly reflects the ground water in a particular hydrogeologic unit at a particular location (33).

Round-robin: Interlaboratory study where a group of laboratories all analyse a subsample from a large homogeneous sample in order to compare their methodology and their accuracy.

Scan: In mass spectrometry, a given range of masses e.g. 50 to 450 a.m.u. or daltons) acquired in a specified time e.g. one second.

SIM: In mass spectrometry, selected ion monitoring. In contrast to the scan mode, only a few masses, e.g. 78,151,153,173, are acquired. This takes only a fraction of a second and allows several acquisition to be performed in one second, enhancing the sensitivity for these ions. Not to be confused with SIMS.

SIMS: secondary ion mass spectrometry- a technique where non-volatile compounds are ionized on a metal surface (16).

Spiked samples: A sample to which a known amount of analyte is added to measure the matrix effects on the analytical methodology. A large sample is divided in two and half is spiked the other one is left intact. Both samples are analyzed in parallel.

Surrogate: A compound which is representative yet different often deuterated or fluorinated compounds) from the target analytes and is added to the sample prior to extraction. Its recovery is indicative of matrix effect.

TAGA: Target Atmospheric Gas Analyser. Mass spectrometer with the source at ambient pressure which allows instant on-site monitoring of atmospheric gases.

TNT: Trinitrotoluene - explosive compound.

Trip blank: A sample of laboratory purified water travelling unopened from and back to the laboratory along with the sample bottles, to find out about possible contamination in transit. See also field blank.

Volatiles: A group of compounds which may be analysed by purging them out of water by a stream of inert gas at room temperature. Their boiling point is below 150°C.

REFERENCES

1. Taylor J.K. (1988). Quality assurance of chemical measurements. Lewis Publishers, Inc. Chelsea, Michigan.

2. Plumb, R. chapter 7, this book.

3. CRC Handbook of Chemistry and Physics. Published yearly by The Chemical Rubber Co. Cleveland Ohio 44128.

4. Montgomery, J.H. and Welkom L.M. 1990). Groundwater Chemicals Desk Reference, Lewis Publ. Chelsea Michigan. 640 pages.

5. The Merck Index 11th Edition 1989, Susan Budavari Editor. Published by the Merck & Co. Inc. Rathway N.J. USA.

6. Aldrich Chemical Company Inc. 1988-89 Catalog Handbook of Fine Chemicals. Milwaukee, WI 53233 USA. 2212 pages.

7. Lesage, S. 1977). Synthesis and Stereochemistry of Unsaturated Lactones related to Fungal Metabolites. Ph.D. Thesis, McGill University, Montreal, Canada.

8. Koehn, J.W. and Stanko J.H. Jr. 1988. Groundwater monitoring. Environ. Sci. Tech., 22:1262-1264.

9. Hughes, B.M., McLellan, R.D., and R.W. Gilham Chapter 5, This book.

10. Priddle, M.W., Lesage S. and Jackson R.E. 1990. Analysis of Oxygenated Solvents in Groundwater by Dynamic Thermal Stripping-GC- MSD. Int. J. Environ. Anal. Chemistry. in press .

11. Swallow K.C. Chapter 2 This book.

12. U.S. Environmental Protection Agency. 1984). Federal Register Part VIII. 40 CFR Part 136. Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule. Friday October 26. 49209).

13. American Chemical Society Committee Report 1983. Principles of Environmental Analysis, Analytical Chemistry, 55:2210-2218.

14. U.S. Environmental Protection Agency. 1987). Test Methods for Evaluating Solid Wastes Physical/Chemical Methods SW-846), Third edition.

15. Swallow, K.C., Shiffrin, N.S. and Doherty P.J. 1988). Hazardous organic compound analysis. Environ. Sci. Technol., 22:136-142.

16. Hass, J.R. and Norwood D.L. 1984. Organic Mass Spectrometry. in Water Analysis, **Vol 3,** Edited by R. A. Minear and L.H. Keith, Academic press, Orlando FL. pp 253-316.

17. Jackson, R.E., Mutch, J.P. and Priddle, M.W. 1990). Persistence of aldicarb residues in the sandstone aquifer of Prince Edward Island, Canada. J.Contaminant Hydrology, 6:21.

18. Lesage, S., Ritch J.K. and Treciokas, E.J. 1990. Characterization of Groundwater Contaminants at Elmira, Ontario, by Thermal Desorption, Solvent Extraction GC-MS and HPLC. Water Pollution Research Journal of Canada . In press.

19. Covey, T.R., Lee, E.D., Bruins, A.P., Henion, J.D. 1986. Liquid Chromatography / Mass Spectrometry. Anal.Chem. 58:1451-1461.

20. Gwka, D.F. and Hiatt, M. 1984). Analysis of Hazardous Wastes and environmental Extracts by GC/FTIR and GC/MS. Anal. Chem. 56:1102.

21. Shafer, K.H. et al. 1984). Analysis of Hazardous wastes by Fused-Silica Capillary GC/FTIR and GC/MS. Anal Chem.56:237.

22. Grisak, G.E., Jackson, R.E. and Pickens, J.F. 1978). Monitoring ground-water quality: the technical difficulties. In Establishment of Water Quality Monitoring Programs, L.G. Everett and K.D. Schmidt, eds.), AWRA, Minneapolis, Minn., pp 210-232.

23. Reilly, T.E., Franke, O.L. and Bennett, G.D. 1989). Bias in ground-water samples caused by wellbore flow. J. Hydraulic Engr. 115:270-276.

24. Lesage, S., Jackson, R.E., Priddle, M.W. and Riemann, P.G. 1990). Occurrence and Fate of Oragnic solvent residues in anoxic groundwater at the Gloucester landfill, Canada. Environ. Sci. Technol., 24:559-566.

25. Cowgill, U.M. 1988). Sampling waters, Principles of Environmental Sampling L.H.Keith, ed.) American Chemical Society, Washington, D.C., pp. 171-189.

26. Barcelona, M.J., Helfrich, J.A., Garske, E.E. and Gibb, J.P. 1984) A laboratory evaluation of ground water sampling mechanisms. Ground Water Monitoring Review, 4:32-41.

27. Barcelona, M.J., and Helfrich, J.A. 1986. Well Construction and Purging Effects on Ground-Water Samples. Environ. Sci.Technol., 20:1179-1184.

28. Robin, M.J.L. and Gillham, R.W. 1987). Field Evaluation of well purging procedures. Ground Water Monit. Rev., 7: 85-90.

29. Barcelona, M.J., Gibb, J.P., Helfrich, J.A. and Garske E.E. 1985. Practical guide to Ground-Water Sampling. Illinois State Water Survey, Champaign, Illinois.

30. Jackson, R.E. and Patterson, R.J. 1982). Interpretation of pH and Eh trends in a fluvial sand aquifer system. Water Resources Research, 18:1255.

31. Baedecker, M.J.. and I.Cozzarelli Chapter 16 this book.

32. Kent, R.T. and Payne, K.E. 1988). Sampling groundwater monitoring wells, Principles of Environmental Sampling L.H.Keith, ed.), American Chemical Society, Washington, D.C., pp. 321-246

33. General Accounting Office GAO). 1988). Ground-water conditions at many land disposal facilities remain uncertain. U.S. General Accounting Office, Washington D.C., 53p.

34. WMS Associates Ltd., Intera Technologies and National Water Research Institute. 1989). Investigation of Suspected PAH Contamination of Groundwater, Newcastle, New Brunswick. Report to the New Brunswick Ministry of the Environment, 29pp., 4 Appendices. WMS file 2988. Fredericton, New Brunswick, Canada.

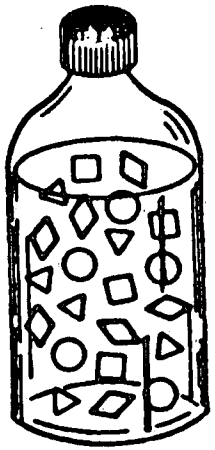
35. Goerlitz D. Chapter 11 this book.

36. Lesage, S. and Lapcevic, P.A. 1990). Differentiation of the Origins of BTX in ground water using multivariate plots. Ground Water Monit. Rev., Spring:102-106.

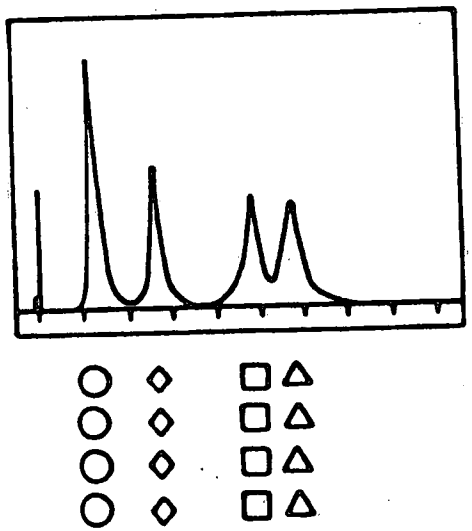
LIST OF FIGURES

COMPONENTS OF A GC/MS SYSTEM

SAMPLE



GAS CHROMATOGRAPHY



MASS SPECTROMETRY

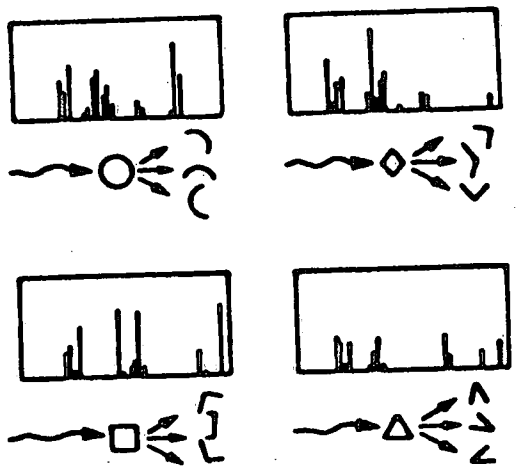
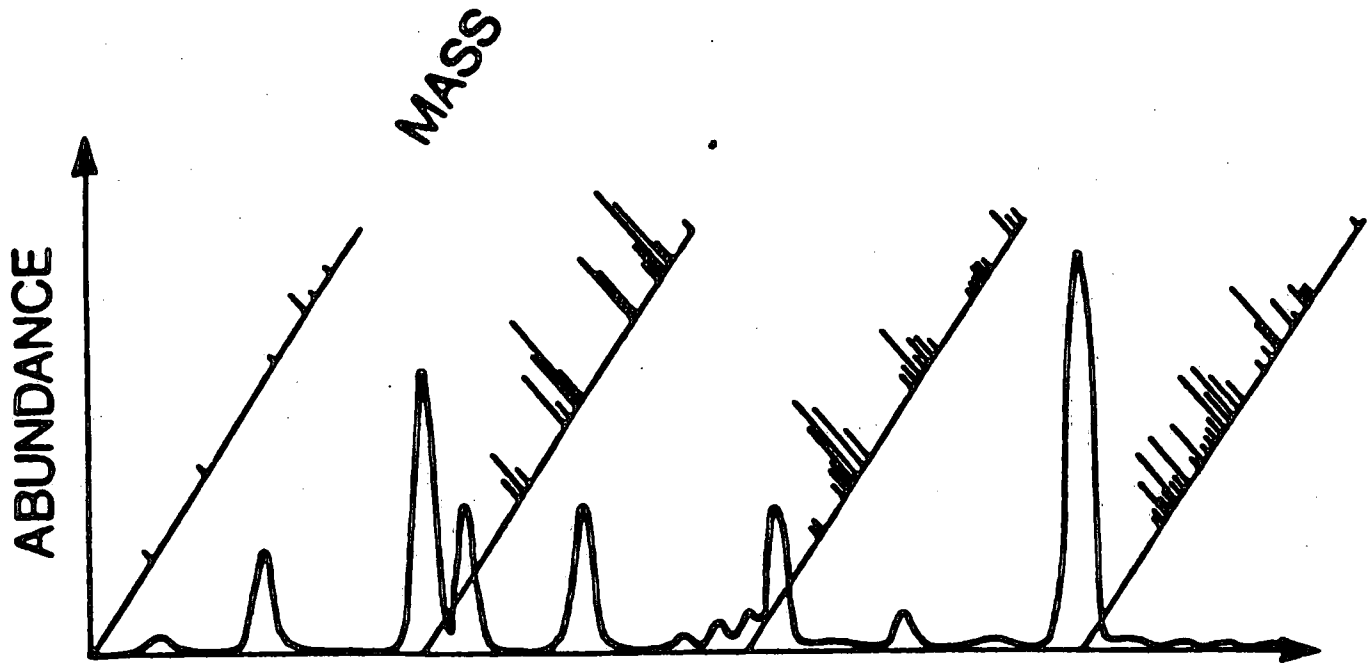


Figure 1

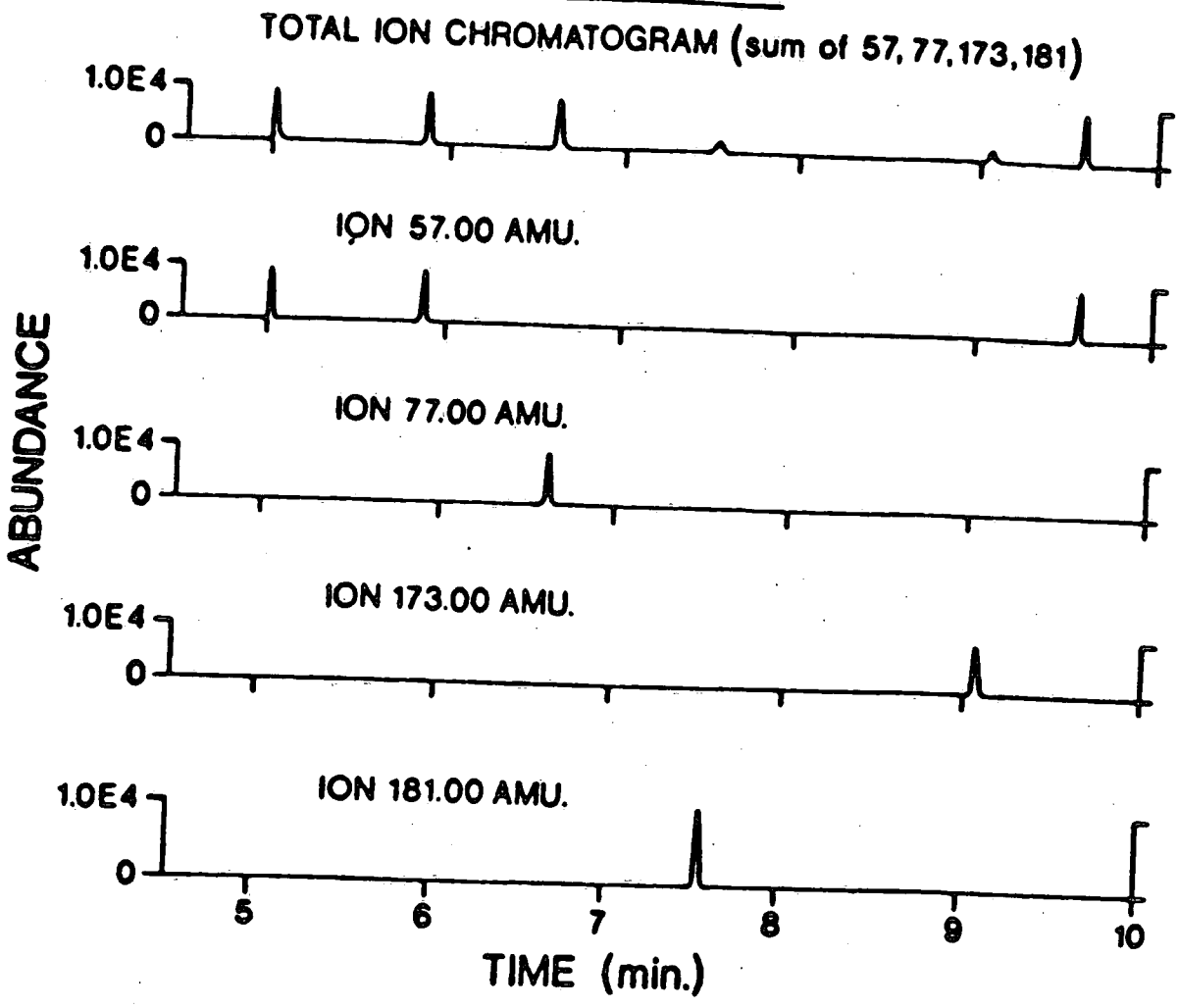


TOTAL ION CHROMATOGRAM

Figure 2

SELECTED ION MONITORING

- ONLY SELECTED IONS ARE ACQUIRED
- MAXIMIZES SENSITIVITY AND SELECTIVITY
- DOES NOT ALLOW THE IDENTIFICATION OF UNKNOWNS



EACH CHANNEL IS A SPECIFIC DETECTOR

Figure 3

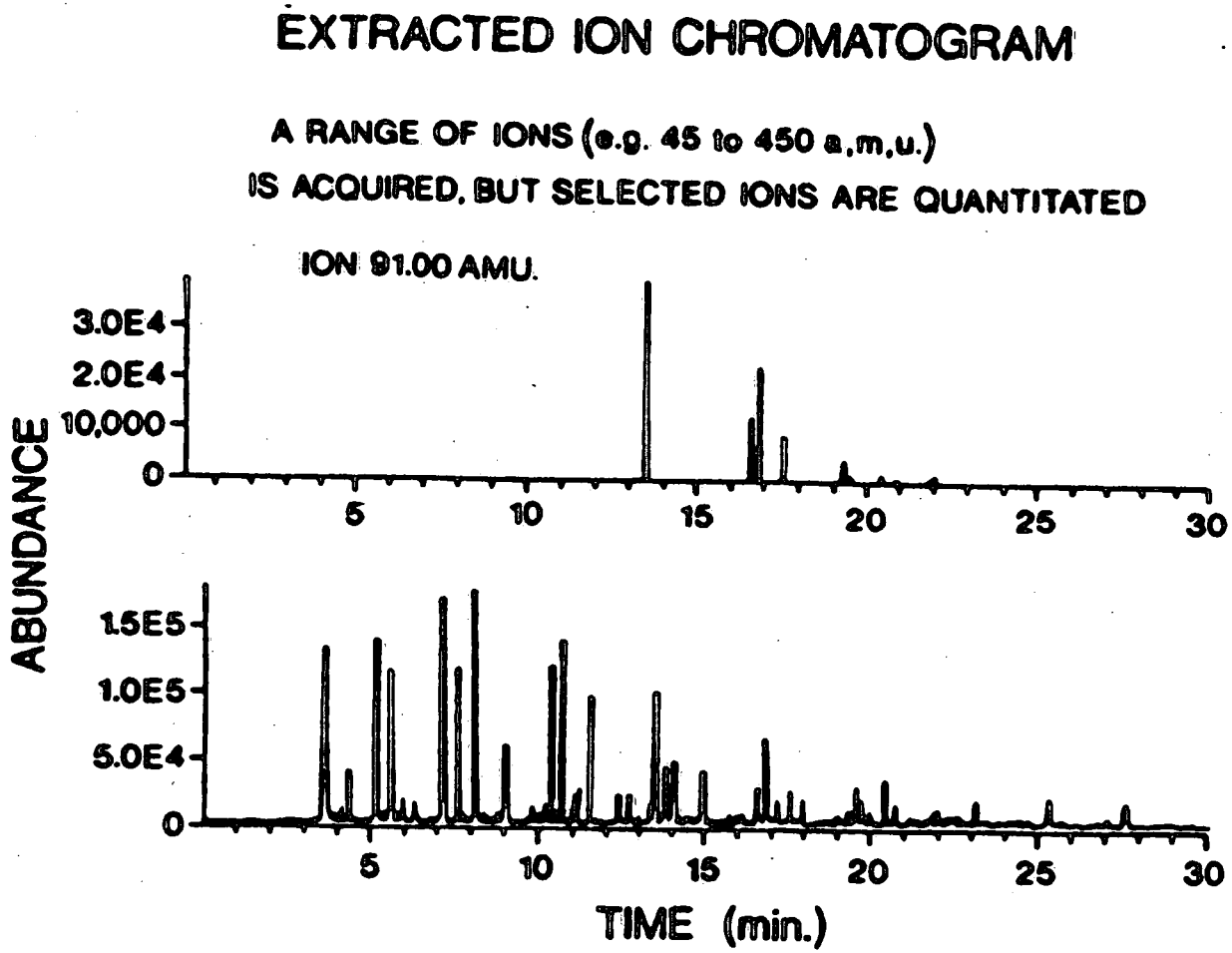
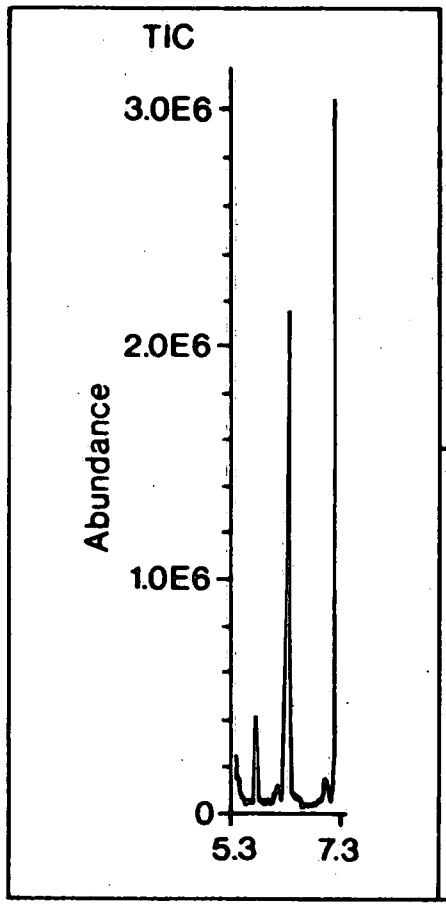

EXTRACTED ION CHROMATOGRAM
A RANGE OF IONS (e.g. 45 to 450 a.m.u.)
IS ACQUIRED, BUT SELECTED IONS ARE QUANTITATED
ION 91.00 AMU.
ABUNDANCE
3.0E4
2.0E4
10,000
0
1.5E5
1.0E5
5.0E4
0
5
10
15
20
25
30
TIME (min.)

Figure 4

1,1 DICHLOROETHANE



	MASS	RT TIME	AREA COUNT	RATIO
QUAN.	63.00	6.32	46886580	
QUAL.	63.00	6.32	15064710	32.13

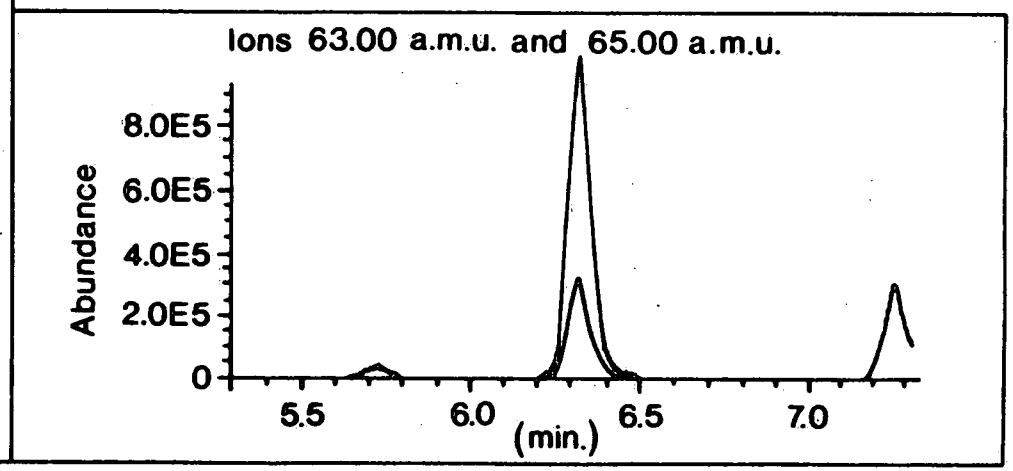


Figure 5

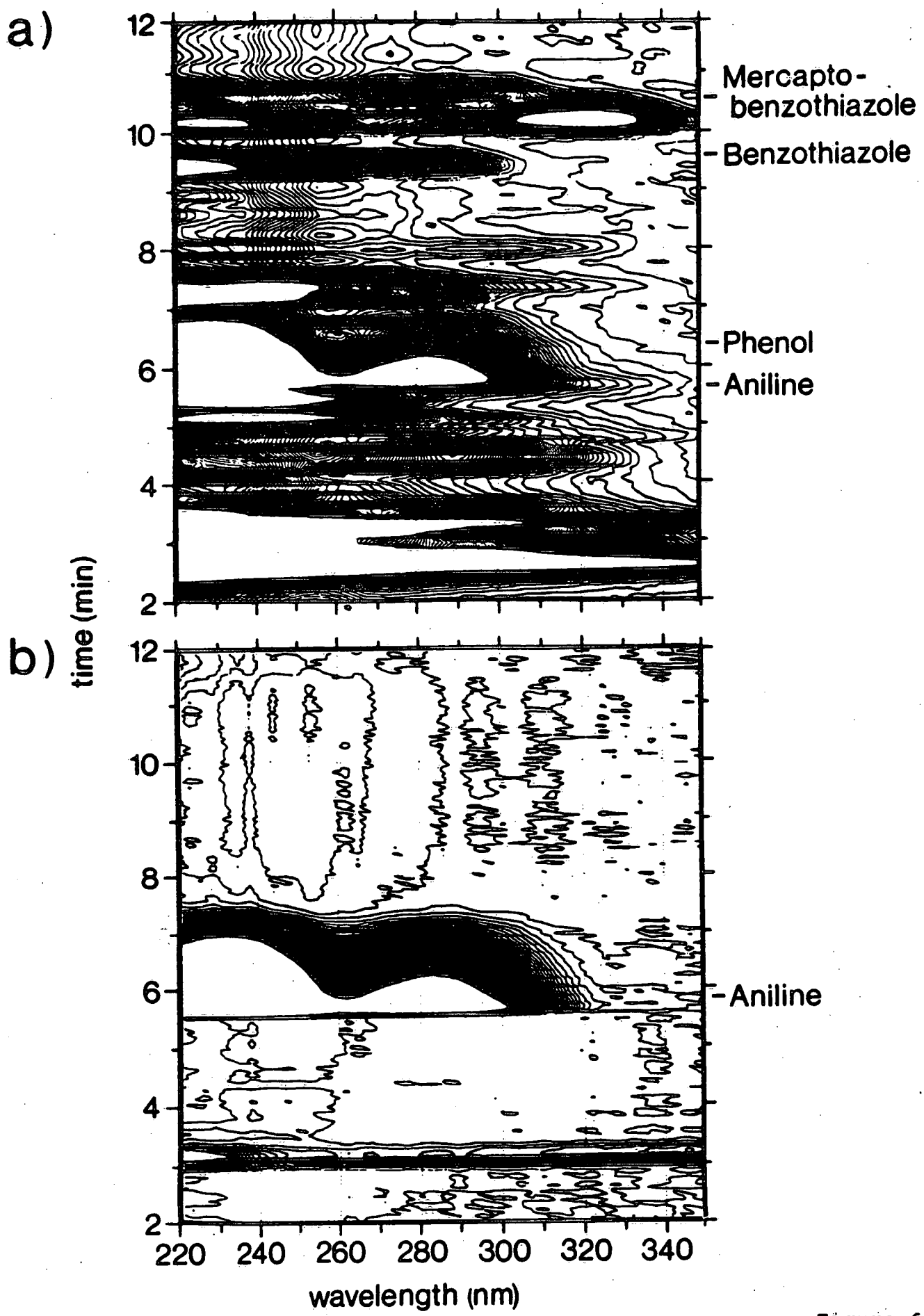

a)
b)
time (min)
12
10
8
6
4
2
Mercapto-
benzothiazole
Benzothiazole
Phenol
Aniline
Aniline
220
240
260
280
300
320
340
wavelength (nm)

Figure 6

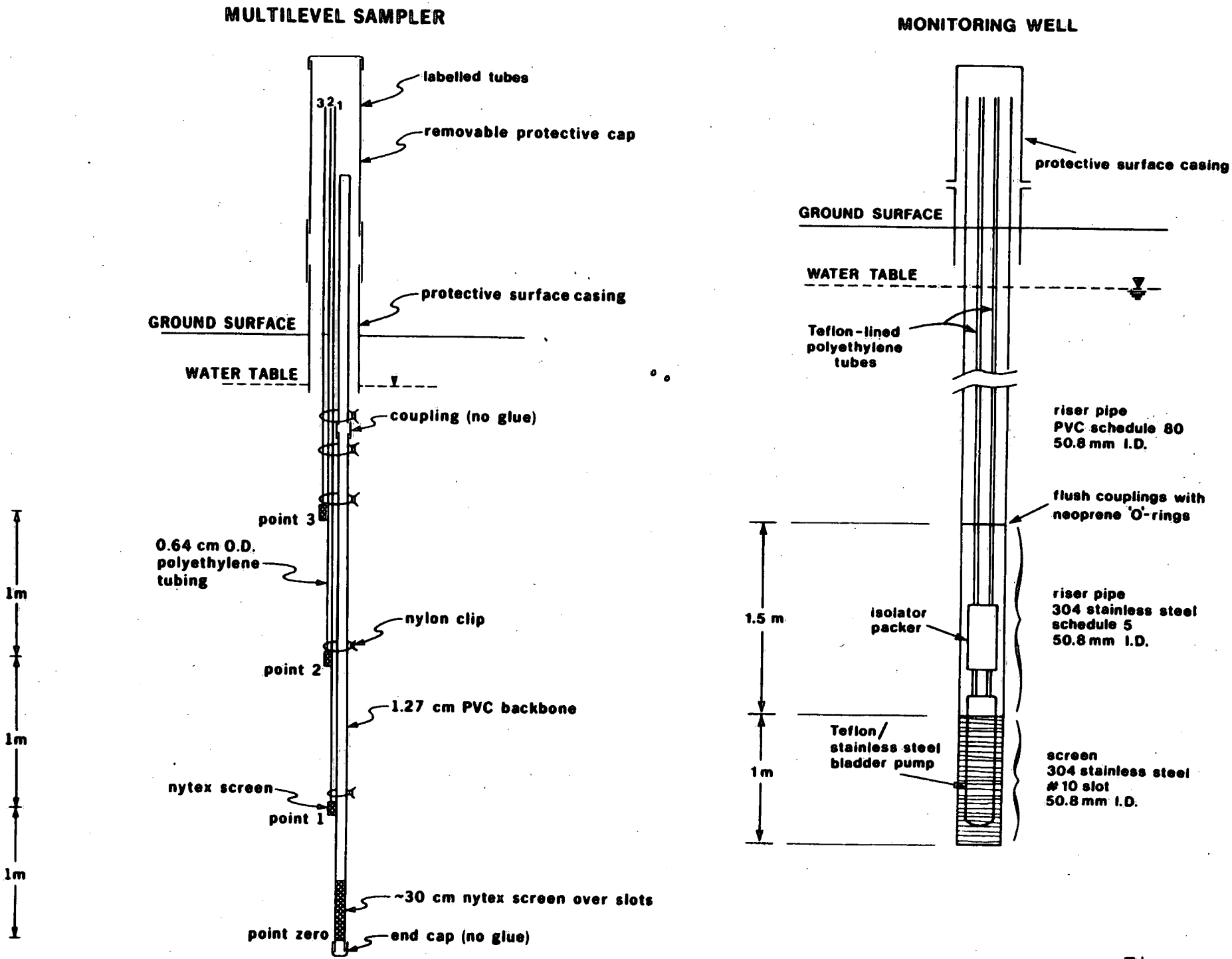

MULTILEVEL SAMPLER
labelled tubes
3 2 1
removable protective cap
protective surface casing
GROUND SURFACE
WATER TABLE
coupling (no glue)
point 3
0.64 cm O.D. polyethylene tubing
nylon clip
point 2
1.27 cm PVC backbone
nytex screen
point 1
~30 cm nytex screen over slots
point zero
end cap (no glue)
1m
1m
1m
MONITORING WELL
protective surface casing
GROUND SURFACE
WATER TABLE
Teflon-lined polyethylene tubes
riser pipe PVC schedule 80 50.8 mm I.D.
flush couplings with neoprene 'O'-rings
1.5 m
isolator packer
riser pipe 304 stainless steel schedule 5 50.8 mm I.D.
Teflon/ stainless steel bladder pump
1 m
screen 304 stainless steel #10 slot 50.8 mm I.D.

Figure 7

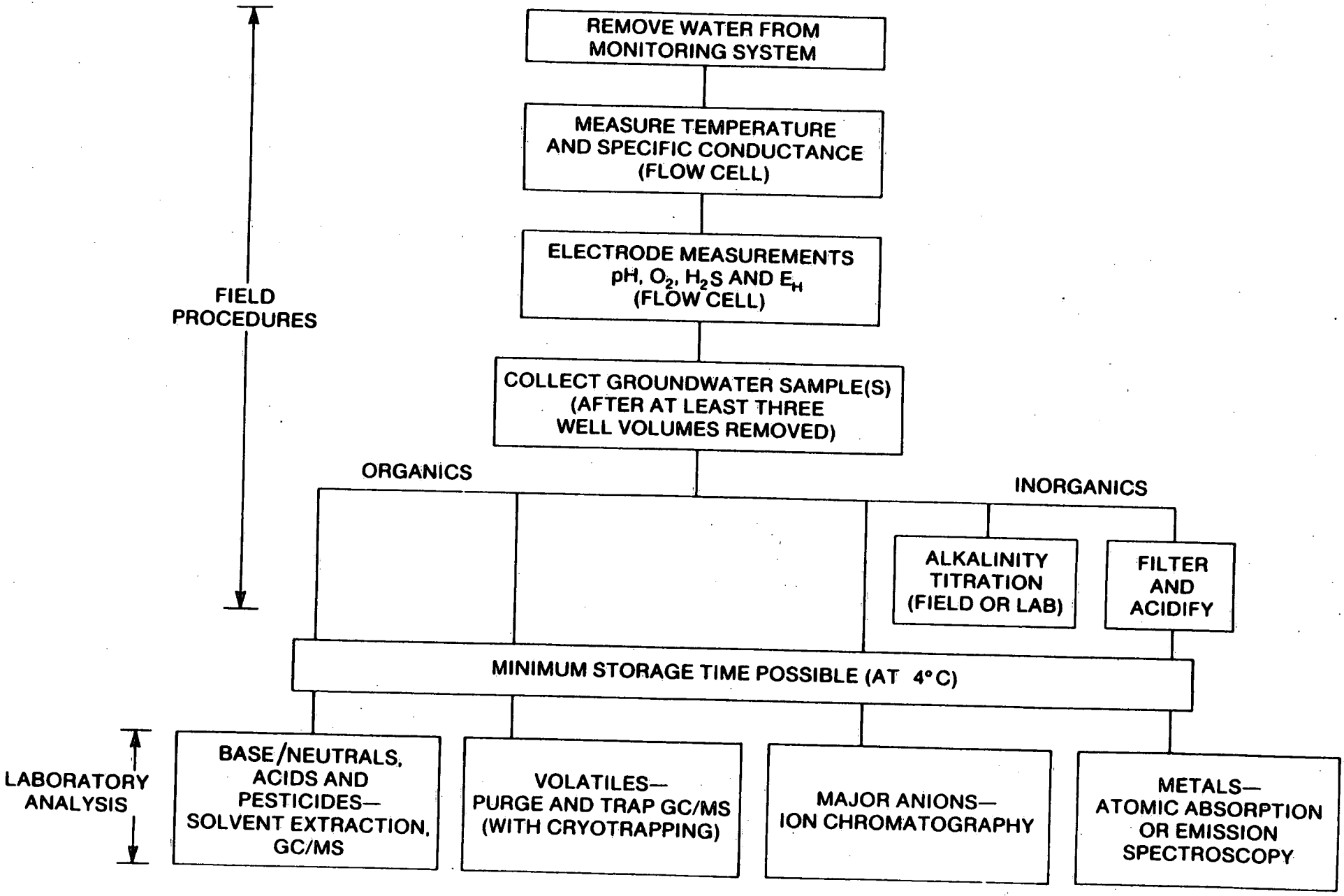
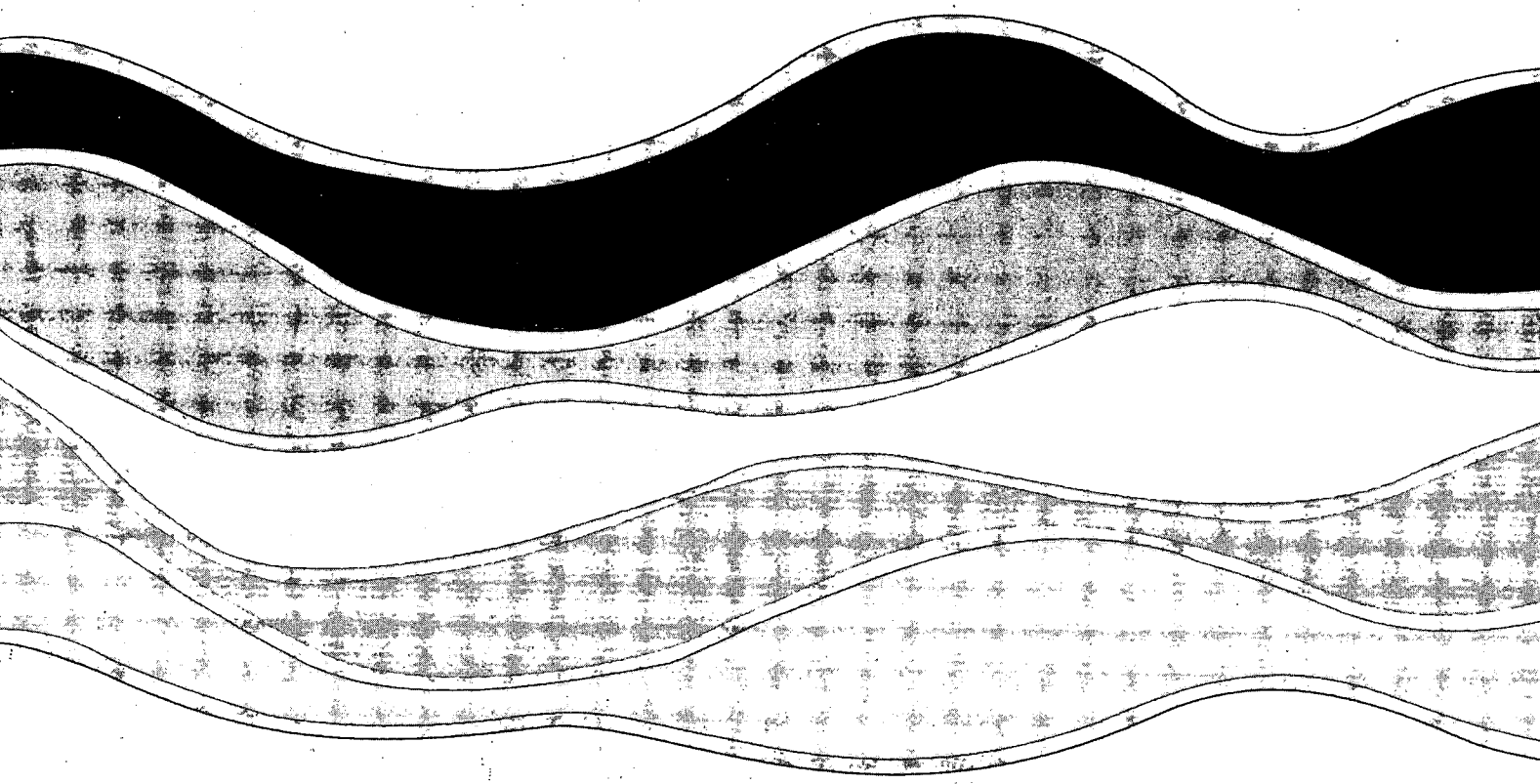

FIELD PROCEDURES
REMOVE WATER FROM MONITORING SYSTEM
MEASURE TEMPERATURE AND SPECIFIC CONDUCTANCE (FLOW CELL)
ELECTRODE MEASUREMENTS pH, O_2, H_2S AND E_H (FLOW CELL)
COLLECT GROUNDWATER SAMPLE(S) (AFTER AT LEAST THREE WELL VOLUMES REMOVED)
ORGANICS
INORGANICS
ALKALINITY TITRATION (FIELD OR LAB)
FILTER AND ACIDIFY
MINIMUM STORAGE TIME POSSIBLE (AT 4°C)
LABORATORY ANALYSIS
BASE/NEUTRALS, ACIDS AND PESTICIDES— SOLVENT EXTRACTION, GC/MS
VOLATILES— PURGE AND TRAP GC/MS (WITH CRYOTRAPPING)
MAJOR ANIONS— ION CHROMATOGRAPHY
METALS— ATOMIC ABSORPTION OR EMISSION SPECTROSCOPY

Figure 8



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Environment Canada Environnement Canada

Canada

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