

## Review

# Methods for the analysis of hazardous wastes

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### ABSTRACT

This review covers the analytical methods for water and contaminated soils at hazardous waste sites. The different methods needed for rapid screening, target compound analysis and in-depth investigations, are presented. Field techniques, which are becoming commonplace, are also discussed.

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### 1. INTRODUCTION

The need to characterize the content of hazardous waste landfills has arisen from the public concern over their potential impact in the surrounding air and water. Certain chemicals deposited in landfills have been known to be potentially harmful if they volatilize in the air or leach in the groundwater.

Until recent years, a comprehensive characterization of chemicals in a landfill was an extremely onerous task. At best, gas chromatographs with an electron capture detector could reveal the presence of some industrial chemicals that were suspected to be present. Concentrations of metals were deter-

mined, one by one, by atomic absorption spectrophotometry.

The advent of gas chromatography–mass spectrometry (GC–MS) and inductively coupled plasma (ICP) greatly increased our capabilities, rekindling the interest in characterizing industrial effluents [1]. It now became possible to analyse replicate samples and address the question of analytical quality control. The fact that it was now possible to analyse samples in triplicate at a more reasonable cost, led to an awareness of the reliability and the limitations of our analytical capabilities. It also uncovered the problems of the representativeness of the samples.

This article discusses the methods that are used for different degrees of investigations: from the

broad screening methods used to characterize the degree of hazard of the waste, and target compound analyses where individual known toxic compounds are sought and quantitated, to methods that are used to for in-depth investigations and potential remediation. Soil, water and non-aqueous phase liquids are considered, but the primary emphasis is placed on leachate from the landfill and contaminated groundwater, because leaching tests are probably the most frequently used methods of characterizing solid wastes and because groundwater is the resource most threatened by hazardous waste sites. Some attention is given to field methods as well as laboratory methods, because the importance of rapid response for the assessment of remediation scenarios is increasingly being recognized.

## 2. SCREENING METHODS USED FOR WASTE CLASSIFICATIONS

Prior to doing any chemical analysis, any information that can be gathered regarding the origin of the waste should be used. Different countries have defined various criteria as to what constitutes hazardous wastes, but a consensus on a certain number of chemicals as hazardous has been reached by the OECD and UNEP [2]. The presence of any component listed in Table 1 is sufficient to classify the waste as hazardous. Some countries utilise concentrations to indicate whether or not waste containing one or more of the substances listed in Table 1 is hazardous, but doing so implies a high degree of monitoring and control which is beyond the means of many countries and hence is not the subject of an international consensus.

In any hazardous waste investigation, the primary need is to establish whether the waste poses an immediate threat to the investigator. In the first analysis, determining whether the waste is flammable, whether it may be mixed with water or whether it is corrosive or radioactive is often all that is necessary to proceed. This type of approach is used by emergency response teams [3] who need to know immediately how to respond to a problem. Their need for precision is not high, but they have to be rapid and correct in their assessment. Methods used include pH and starch iodine indicator papers, simple flame tests, portable gas analysers (OVA<sup>TM</sup>) and Geiger counters. Many of the methods have been

borrowed from the occupational health sector in industry.

The laboratory at the receiving dock of a hazardous waste landfill or incinerator uses much of the same technology in its decision to accept or reject a shipment of waste [4]. In addition, these laboratories have equipment such as GC, GC-MS and ICP that allow for more in-depth investigation or analyses for specific chemicals of interest such as polychlorinated biphenyls (PCBs).

Many of the screening methods, which were developed initially for the characterization of sewage effluents, are compiled in a handbook [5]. It covers parameters such as total dissolved solids, total organic carbon (TOC), biological oxygen demand (BOD), oil and grease, total phenols, cyanide, sulfate and nitrate. This handbook also contains specific methods for heavy metals such as lead, mercury and zinc. Many of the parameters are bulk or indicator parameters. They do not pertain to a single chemical but rather are used to give a comparative measure of the degree of contamination of a sample and its possible impact on the environment, and to indicate how it should be treated.

These tests are relatively inexpensive and may be performed very rapidly. Some of them can be easily done at the field site (pH, oil and grease, methane gas, total PCBs colorimetric test) and allow for a good primary response to describe the nature of the waste. Care must be exerted however in the interpretation of the results of some screening methods. Possibly the worst case is the analysis for total phenols using the colorimetric technique based on condensation with 4-aminoantipyrine. Although it is stated that only non-*p*-substituted phenols will produce the colour, attempts to correlate this with other techniques, such as HPLC, indicate that there are other discrepancies, mostly because phenol is used as the only reference standard [6]. In hazardous wastes, the presence of amines such as aniline interferes with the test [7]. TOC analysis should be used with caution in any samples where a large portion of the organic carbon is due to volatiles, because they will be largely lost when the sample is purged initially to remove the inorganic carbon as CO<sub>2</sub>. Alternate methods similar to purge-and trap have been developed but are seldom used by commercial laboratories [8].

Waste generators must now assess the leaching

TABLE 1

## INTERNATIONAL LIST OF HAZARDOUS SUBSTANCES

Adapted from ref. 2.

Code No.	Hazardous constituent
C 1	Beryllium and its compounds
C 2	Vanadium compounds
C 3	Chromium VI compounds
C 4	Cobalt compounds
C 5	Nickel compounds
C 6	Copper compounds
C 7	Zinc compounds
C 8	Arsenic and its compounds
C 9	Selenium and its compounds
C 10	Silver compounds
C 11	Cadmium and its compounds
C 12	Tin compounds
C 13	Antimony and its compounds
C 14	Tellurium and its compounds
C 15	Barium and its compounds; excluding barium sulfate
C 16	Mercury and its compounds
C 17	Thallium and its compounds
C 18	Lead and its compounds
C 19	Inorganic sulfides
C 20	Inorganic fluorine compounds; excluding calcium fluoride
C 21	Inorganic cyanides
C 22	Lithium, sodium, potassium, calcium, and magnesium as metals
C 23	Acidic solutions or acids in solid form
C 24	Basic solution or bases in solid form
C 25	Asbestos as dust or fibres
C 26	Phosphorus and its compounds; excluding mineral phosphates
C 27	Metals carbonyls
C 28	Peroxides
C 29	Chlorates
C 30	Perchlorates
C 31	Azides
C 32	Polychlorinated biphenyls and terphenyls
C 33	Pharmaceuticals or veterinary medicines
C 34	Biocides and phyto-pharmaceutical substances (e.g., pesticides)
C 35	Infectious substances (e.g., viruses)
C 36	Creosotes
C 37	Isocyanates, thiocyanates
C 38	Organic cyanides (e.g., nitriles)
C 39	Phenols
C 40	Halogenated solvents
C 41	Organic solvents, non-halogenated
C 42	Organohalogen compounds excluding inert polymers
C 43	Aromatic compounds; polycyclic and heterocyclic
C 44	Aliphatic and other nitrogen organic compounds
C 45	Aromatic amines
C 46	Ethers
C 47	Explosives
C 48	Organic sulfur compounds
C 49	Polychlorinated dibenzofurans
C 50	Polychlorinated dibenzo- <i>p</i> -dioxins
C 51	Hydrocarbons and their oxygen, nitrogen or sulfur compounds

potential of their wastes and therefore their potential for groundwater contamination. Different governments have developed standardized protocols that must be followed by all industries within their territories. In the USA, the Environmental Protection Agency (EPA) has established standards for the treatment of restricted wastes and leaching procedures to evaluate the leaching potential of hazardous wastes. The Toxic Characteristic Leaching Procedure (TCLP) is designed to determine the leachability of metals, pesticides, semi-volatile and volatile organic compounds [9]. The leaching solution is dilute acetic acid. The leachate is then analysed using the SW846 methods [10]. In Canada, the province of Ontario has well defined pieces of legislation regarding the classification and the leaching of hazardous wastes, known as Regulation 309 [11]. It also advocates the use of a dilute acetic acid solution (0.5 M) to extract the wastes. The different types of leaching tests used world-wide have been described in a compendium report [12].

### 3. TARGET COMPOUND ANALYSIS

At the next level of response, samples are sent to the laboratory for characterization. The samples generally consist of water, soil or other solids, and oily waste. They are screened for the possible presence of chemicals that are known to be toxic and to be used in the environment. The reason for this approach is that it is easier and less expensive to determine, for example, if there are PCBs in a sample than to try to identify all the possible contaminants in the samples. Lists of priority substances, substances that are known to be toxic or to be generally deleterious to the environment and to human health, have been compiled. The best known and most comprehensive list is known as Appendix IX [13]. Appendix IX is a list of 222 compounds and is the shortened form of Appendix XVIII, which is a list of over 400 target chemicals contained in an appendix to the US EPA Hazardous Substance Act known as RCRA (Resource Conservation and Recovery Act). The list was shortened because almost half of the compounds on the original list could not be measured with any degree of accuracy using the existing methodology [14,15].

The analytical methods suggested by the US EPA for these compounds are contained in a manual

generally referred to as the SW846 manual [10]. The SW846 manual was developed after the Effluent Guidelines Methods which were the first promulgated methods (1979, revised in 1984) for the analysis of water, and wastewater, including groundwater [16]. In the Effluent Guidelines Methods, the contaminants were divided into several analytical groups such as volatiles, base-neutrals and acids, pesticides (organo-chlorine) and PCBs, and metals. The methods are based on chromatography including GC, high-performance liquid chromatography (HPLC) or GC-MS for the organic compounds, and on spectroscopy, atomic adsorption (AA) or ICP for the metals. The volatiles are analysed by purge-and-trap-GC, whereas the semi-volatile analytes are extracted by dichloromethane and the extracts are analysed by gas chromatography with a selection of detectors.

The same framework is used for the SW846, except that it is recognized that many of the samples require some other form of preconcentration or cleanup, before they can be measured by the same methods as the effluents are. Much more autonomy is given to the individual analyst because of the diversity of matrices encountered. An excellent review of the SW846 methods and of their capability was written by Parr *et al.* [14]. Therefore, they will only be discussed briefly here.

Only the USA have proclaimed such a comprehensive list of methods. However, researchers and government authorities have designated target compounds and many methods, other than the US EPA methods, have been used world-wide. Those methods will be discussed here in parallel and grouped according to target groups of compounds, in water or liquids and soil or solids.

#### 3.1. Volatiles

This is the first analytical group to be considered in dealing with liquid wastes. It covers chlorinated methanes and ethanes and the aromatic components of light petroleum distillates (benzene, toluene, xylenes, *etc.*). For water, purge-and-trap is the most used technology (ref. 10, method 5030) and was borrowed from the Effluent Guidelines Methods. Purge-and-trap, initially developed by Bellar and Lichtenberg [17], consists of bubbling gas through an aqueous sample to strip it of its most volatile components. The gas is passed through a

solid sorbent such as Tenax [16] or Carbotrap [18] onto which the analytes are adsorbed, then thermally desorbed on-line into GC or GC-MS. A combination of electron-capture and Hall detectors has been used for the simultaneous measurement of chlorinated and aromatic hydrocarbons [19].

Some investigators have used adsorption onto cartridges followed by thermal desorption [20,21]. Sorption from water directly onto cartridges allows for sampling groundwater down-hole [22]. Micro-cartridges [23] and uncoated capillary columns [24] have also been used instead of polymeric sorbents. Adsorption on cartridges is also used for air samples and volatile organic sampling trains (VOST) at incinerators where a given amount of air is pumped through the sorbent, which is then thermally desorbed [10 (method 3720), 25]. Purging directly onto a capillary column with whole column cryotrapping, *i.e.* cooling down the whole gas chromatograph to condense the analytes, was used successfully by Pankow and Rosen [26] for petroleum contaminated water. The use of a trap to desiccate the hot gas stream before it reaches the chromatograph is essential to prevent ice formation in the capillary column.

Purge-and-trap is the most often employed method in the USA, but in other jurisdictions and for samples where excessive foaming occurs, headspace analysis is also often used [10,27–31]. Headspace analysis is more conveniently conducted in the field. Groundwater samples are rapidly screened in the field using partially filled vials sealed with a septum. A volume of the headspace is injected into a portable gas chromatograph equipped with a photo-ionization detector such as the Photovac™. Detection limits down to 1 µg/l have been obtained for benzene [32]. Liquid-liquid extraction with pentane [33] or hexane [34] followed by injection into a GC or GC-MS has been used for the measurement of halogenated hydrocarbons and aromatic hydrocarbons in landfill leachate.

Solvents such as 1,4-dioxane or tetrahydrofuran, which are highly soluble in water, are not efficiently analysed by purge-and-trap or headspace analysis because they do not partition sufficiently into the gas phase. For such samples, the technique of dynamic thermal stripping (DTS) has proven effective [35]. DTS is similar to purge-and-trap, but the purging is done at a higher temperature onto a cartridge, which is thermally desorbed subsequently.

More unusual is the use of HPLC to measure benzene, toluene, ethyl benzene and xylenes [36]. The separation was done on a C<sub>18</sub> column eluted with 75% methanol and 25% water. The detection limit was quoted as 5–10 µM.

Soil samples present a special challenge in volatile analysis. Any attempt at homogenizing or drying the sample will result in significant loss of analyte. The samples are therefore analysed wet and the dry weight is determined on a separate aliquot. For purge-and-trap analysis, the sample is first dispersed in polyethylene glycol or methanol. An aliquot of the sample extract is then added to water and analysed by purge-and-trap [10 (method 5030)]. Some investigators have simply added water to a soil sample in the purging vessel [37,38]. The sorbent desorption has most often been thermal, but extraction with CS<sub>2</sub>, a method borrowed from the occupational health sector, has also been used [38].

Soil vapour analysis can also be conducted in the field. The headspace in a specially designed monitoring well is sampled and analysed using a gas chromatograph with a photo-ionization detector, which can measure most solvents, from aromatic hydrocarbons to chlorinated hydrocarbons. The limitations of the technique have been described by Hughes *et al* [39]. As in any headspace technique, the control of the sample temperature, is crucial to the accuracy of the results. There are obviously inherent problems to achieving temperature control in the field. Excellent replication (10% R.S.D.) can be attained if attention is paid to the potential leaks in the system and to the integrity of sampling syringes. Other investigators have used a mobile laboratory equipped with gas chromatographs where soil gas samples taken from stainless steel hollow probes could be analysed on site [40].

### 3.2. Semi-volatiles

Semi-volatiles is an operational term coined by the US EPA to designate compounds that are not sufficiently volatile to be analysed by purge-and-trap-GC, but could be volatilized in a hot injector and analysed by GC. The compounds range in volatility from dichlorobenzenes to benzo-*[ghi]*-perylene. The Effluents Guidelines Protocol [16] subdivides the semi-volatiles into three main groups: the base-neutrals, the acids, and the organo-chlorine pesticides and PCBs. Base-neutrals and acids are

TABLE 2

## SAMPLE EXTRACTION TECHNIQUES FOR SEMI-VOLATILES, SW846 METHODS [10]

Method	Matrix	Description
3510	Aqueous	Separatory funnel liquid–liquid extraction with dichloromethane
3520	Aqueous	Continuous liquid–liquid extraction with dichloromethane
3540	Soils, sludges and wastes	Soxhlet with acetone–hexane (1:1) or toluene–methanol (10:1) or dichloromethane
3550	Soils, sludges	Sonication with same solvents as in 3540

separated by the extraction at pH 10 and pH 2, respectively, then analysed by GC–MS. The base-neutral fraction contains compounds such as polyaromatic hydrocarbons, phthalate esters, chlorinated ethers and nitrosamines. The acid fraction contains phenol, methyl phenols and chlorinated phenols. The pesticides and PCBs are extracted separately at neutral pH and the final analysis is conducted by GC with an EC detector. The SW846 equivalent to this method is method 8270, which describes the GC–MS determination [10]. The difference is mainly in the number of analytes for which the method is validated and in the alternate sample preparation techniques (Table 2).

As was touched upon in the screening test section, the analysis for phenols can be a very challenging task especially in complex matrices. When dichloromethane is used, emulsions are often generated which reduce the efficiency of extraction. Alternate solvents have been tried; benzene was found not to be efficient and butyl acetate entrained too many co-extractives. The best results were obtained with diethyl ether although many laboratories might be reluctant to use it because of its high volatility and instability [41].

Alternately, phenols have been analysed by HPLC using electrochemical [42–44], UV detection [45–47] or both [48–50]. The electrochemical detector has not received as wide acceptance as it could, probably because of the instability and maintenance requirements of the early models. The selectivity and sensitivity of that detector make it an invaluable tool in monitoring ionizable molecules in complex matrices. HPLC with UV detection at 202 nm was also proposed for rapid screening of 32 priority pollutants [51]. The method did not gain widespread acceptance, probably because of the difficulty of working at such a low wavelength.

Sorption on cartridges followed by solvent desorption has also been used as a sample preconcentration technique. In a study where naphthalene was the only analyte, Borden and Bedient [52] passed 100 ml of an aqueous sample through a C<sub>18</sub> Sep-Pak (Waters/Millipore) and desorbed the analyte with dichloromethane before analysing it by GC. More often the adsorption on cartridges has been followed by thermal desorption directly into a GC–MS [53–55]. In such cases the sorbents have been either Tenax or Carbotrap (Supelco) which are thermally stable. Dynamic thermal stripping instead of direct adsorption has also been used [7,55]. Dynamic thermal stripping is best described as purge and trap at a higher temperature and is a direct extension of the method used for volatiles. The technique cannot be used for very high boiling compounds, but has been successfully used up to the boiling range of pyrene.

A modified thermal-desorption–GC–MS system, capable of analysing PCBs in soils and soil extracts, has been devised [56]. It consists of a thermal probe that is put in direct contact with the soil sample. A 3.5-m capillary column is housed in a piece of tubing with a coil heater instead of the conventional GC oven. For quantitative analysis, the soil sample must be extracted first with hexane, which is vaporized by the probe. The instrument is battery powered and therefore can operate in the field.

### 3.3. Inorganic compounds

The analysis for inorganic salts and metals at hazardous waste sites has received less attention, because the methods used vary less for complex matrices than those for organic compounds. Ion chromatography has revolutionized the way most anion analyses are conducted [5]. Cations may also be determined by ion chromatography, but are most of-

ten analysed as the metals by either AA or ICP [5,10]. For complex matrices, directly coupled plasma (DCP) is often preferred because it is less subject to interferences and will accept samples with higher organic content [57,58]. X-Ray fluorescence spectrometry was used to measure metals in leachate from wood fly ash [59].

The methods for metals in aqueous or solid matrices differ mostly by their acid digestion procedures. Depending on whether the sample will be introduced by in a flame or graphite furnace AA or an ICP detector, the initial digestion is done in nitric acid, followed by a second hydrochloric acid digestion for the flame instrument. Hydrochloric acid cannot be used in the graphite furnace. The methods are adequate for aqueous samples, most soils and sediments and sludges. Some waste materials, such as oil base paints, can cause difficulty and the analysts are always cautioned to verify the results by accompanying the samples with suitable spiked samples to prevent bias due to interferences. The digestion procedures are often adjusted by the analyst to cope with specific interferences, but these adjustments are not considered significant alterations and are seldom published as separate methods. An exception to this was the publication of an alternate preparation procedure for chromium in spent ores with the use of fusion with sodium carbonate and sodium peroxide instead of the digestion in nitric acid [60]. The concentrations reported were an order of magnitude higher with a method derived from that of the American Society for Testing of Materials (ASTM) than with the SW846 method. The most suitable methods varies depending on whether the hazardous waste resembles the original product or it has been mixed with a substantial amount of soil and water.

Artifacts due to sampling equipment and filtration of samples in the field have also been identified. Sampling devices which cause a lot of sample turbidity led to less reproducible results [61]. While it is customary to filter all groundwater samples for metal analysis, discrepancies of up to an order of magnitude can be found in unfiltered compared to filtered samples [62]. If the data is to be used for exposure assessment, whether filtered or unfiltered samples should be used remains a topic of discussion. Retaining the redox environment from which the samples are taken is also important in obtaining representative results.

Field methods are very important for inorganic constituents that are subject to alterations in the presence of oxygen. Alkalinity, dissolved oxygen, hydrogen sulphide, ferrous iron must all be measured in the field to get an accurate reflection of the groundwater condition [63]. A field-portable X-ray fluorescence spectrometer is now available. Its use has now been investigated for the rapid screening of metals and offers great potential for on-site analysis [64]. It has been used in industries such as steel mills, foundries and even the petroleum sector. It is not as popular in the environmental field because it may not be as sensitive as other methods. However, since high concentrations of contaminants are usually present at hazardous waste sites, very sensitive detectors are not necessary [65].

#### 4. IN-DEPTH INVESTIGATIONS

In spite of all the activity at hazardous waste sites, few detailed accounts of contaminants other than priority pollutants have appeared in the refereed literature. One of the first of such investigations described the organic contaminants near dump sites at Niagara Falls, New York. Compounds were identified using solvent extraction and vapour stripping followed by GC-MS [66]. Solvent extraction of contaminated groundwater and soils followed by GC-MS, accounts for almost all the analytical methods in these investigations [33, 67–71], but Reinhart *et al.* added derivatization of the acid fraction with diazomethane to improve the chromatography of phenols and carboxylic acids [33].

In spite of its inability to identify unequivocally many of the compounds, the GC-MS trace and spectra were still useful in helping to trace the source of a groundwater plume that was potentially emanating from two adjacent landfills [72]. In some investigations, dynamic thermal stripping or adsorption onto cartridges followed by thermal desorption was substituted for solvent extraction to prepare the samples, but GC-MS was still the main technique used to identify the compounds [7,44].

Alternate techniques were employed by scientists of the US Geological Survey to characterize fully their study sites. Pereira *et al.* [73] used probe distillation with high-resolution MS in addition to GC-MS to identify the organic bases derived from coal tar wastes. Goerlitz, a pioneer in the field of

groundwater contamination at hazardous waste site, was the first to advocate the use of HPLC at the site, to measure phenolic compounds at coal tar contaminated sites [74,75] and to look at compounds that were possible indicators of microbiological activity rather than only the contaminant themselves [76]. At the Cape Cod site, Barber [58] used a large variety of methods to characterize the extent of groundwater contamination: closed loop stripping, purge-and-trap analysis, liquid-liquid extraction and solid phase extraction onto *n*-octyl silica and XAD-8 resin were used as isolation methods. Derivatives were made to analyse for anionic surfactants by electron-capture negative ionization mass spectrometry. Linear alkyl benzenesulfonates were analysed by HPLC with a fluorescence detector. XAD isolates were also subjected to <sup>13</sup>C NMR and infra-red analysis as an attempt to identify the surfactants better.

Attempts were made to characterize the molecular weight distribution of groundwater contaminants at a Canadian site. Barker *et al.* [77] used dialysis to separate the DOC according to molecular weight groups, and then used IR to get an indication of the functional groups present within the different fractions and compared it to spectra of fulvic acids [77].

HPLC-MS was used by Ho *et al.* [78] to solve an analytical problem that had received fairly little attention. It is not possible to distinguish between diphenylamine and its carcinogenic N-nitroso derivative because of the thermal instability of the latter. They were able to prove the absence of N-nitrosodiphenylamine in a soil sample from a dumpsite although it contained a large amount of diphenylamine. Attempts have been made to characterize the non-extractable fraction of landfill leachate using anion-exchange chromatography-particle beam-MS and ICP-MS. Although good quality spectra were obtained, few compounds could be identified because they could not be matched with spectra contained in computerized libraries [79]. This is not surprising because these have been the result of GC-MS analyses. As the techniques of particle beam and thermospray-MS gain popularity, their usefulness should increase. Also, more complementary techniques such as FT-IR and ICP-MS will be needed to provide more structural information on the unknowns.

## 5. CONCLUSIONS AND FUTURE DIRECTION

Compared to the total worldwide effort in environmental analytical chemistry, there have been, in effect, relatively few attempts at fully characterizing hazardous wastes. Reports still routinely contain statements such as: "only 30% of the contaminants could be identified, the rest are suspected to be high-molecular-mass or polar material". This phrase summarizes what the agenda of the analytical chemists should be in the next decade. There is a need to complement GC-MS with techniques that will allow the measurement of polar and higher-molecular-mass compounds. Only a few references could be found mentioning the use of HPLC-MS for hazardous wastes, although the technique is more than 10 years old. GC-FT-IR has not gained wide acceptance as an environmental analytical tool either, mostly because of its lack of sensitivity. This is not a problem at hazardous waste sites where high concentrations of analyte usually prevail. As the need to remediate highly contaminated sites is increasingly recognized as the priority, more emphasis will be placed on finding suitable cost effective methods to analyse their chemical constituents.

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