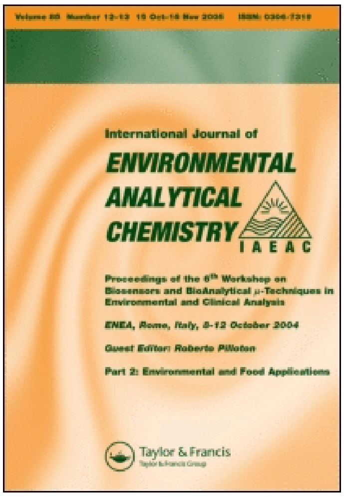

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MULTI-ELEMENT ANALYSIS OF LANDFILL GAS BY ICP EMISSION AND MASS SPECTROMETRY

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Methodology for the determination of trace elements in landfill gas by inductively coupled plasma emission and mass spectrometry is described. The approach is based on direct injection of landfill gas into the ICP using a simple gas sampling manifold. Chlorine and sulphur were quantified in landfill gas by ICP-OES while Sn, Mg, Cu and Zn were measured by ICP-MS. Due to the complex chemical composition of landfill gas, measurements in both emission and mass spectrometry were compromised by spectral interferences. The possibility for multi-element analysis of landfill gas samples based on the use of aqueous standard solutions was demonstrated.

Keywords: Landfill gas; ICP-MS; Chlorine; Sulphur; Trace metals

INTRODUCTION

Landfill gas is an end product of the decomposition of organic wastes in landfill sites and is emitted extensively to the atmosphere [1]. The composition of landfill gas is highly variable and depends on the type of waste amongst other factors such as age of the waste and climate [2]. In general, emission of landfill gas has to be controlled as it is potentially toxic, flammable, explosive and contributes to the greenhouse effect.

Flaring of gas has been the most common option used to control emissions of landfill gas. This process involves combustion at high temperature, objectives being the safe disposal of flammable constituents and odour control [1]. Combustion products from flaring can have adverse environmental impacts and health risks, therefore, full chemical characterisation of landfill gas become necessary. It is projected that there are up to 200 trace constituents in landfill gas [3] including halogenated and sulphonated compounds which may produce highly acidic and aggressive derivatives such as HCl, HF and H_2S [2,3]. Volatile organo-metallic compounds and hydrides such as *n*-butylmethyltin hydride, dimethyl telluride and dimethyl mercury have been detected in landfill gas emissions [4–6]. Volatilisation of these organo-metallics could

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result in substantial emission of metals into the atmosphere where the species could be transformed into inorganic aerosols or precipitates [5,7,8]. Such processes could significantly affect biogeochemical cycles within the environment now and in the future [7].

Gas chromatography (GC) or gas chromatography-mass spectrometry (GC/MS) is often used to estimate the emission of individual chemical species in the landfill gas [8,9]. However, as landfill gas analysis by GC is relatively time consuming, there is a need for development of more rapid and simplified analytical approaches, particularly in the context of screening [8]. ICP emission and mass spectrometry have been extensively developed and used for multi-element analysis of environmental samples [10–12]. In the context of landfill gas analysis, however, there have been few reports on direct element analysis [13–16]. Stoddart *et al.* [17] reported the determination of organo-chlorine in landfill gas samples based on direct gaseous injection into ICP-OES equipped with far UV detection capability [12]. Pecheyran *et al.* analysed volatile organo-metal species in the air (Pb, Sn, Hg and Se) at the sub-pico-gram level by use of cryofocusing and GC-ICP-MS [18,19]. Hyphenated approaches based on GC/MS and GC coupled to ICP have been reported for analysis of volatile organo-metallic species in landfill gas [6,20,21]. Feldman *et al.* [20] identified organo-metallic species of Se, Te, Hg and Pb at the $\mathrm{ng\,m^{-3}}$ level and As, Sn, Sb and Bi at the $\mathrm{\mu g\,m^{-3}}$ level. These GC-ICP-MS based approaches, like GC-MS, are, however, unsuited to rapid screening. Hence, in this study the possibility of developing simple methodology based on direct gaseous injection into ICP emission and mass spectrometry is reported. A key aim of work is to explore the use of aqueous standard solutions for the instrument calibration.

EXPERIMENTAL

Sample Collection and Gas Standards

Landfill gas samples were collected from the L-field site operated by Shanks & McEwans Waste Services (Milton Keynes) [5]. Gas samples were directly pumped into an electroplated stainless steel Gresham tube or a Tedlar bag (SKC Inc., USA) using a stirrup pump. Analysis was typically performed within a week of sampling. A gas standard (1000 ppm ethyl-chloride in a 40 : 60 mixture of carbon dioxide and methane gas; BOC; Guildford, UK) was used in method development along with aqueous standards for chlorine ($500\,\mathrm{mg\,l^{-1}}$ HCl, Aristar grade, BDH, UK) and sulphur ($20\,\mathrm{mg\,l^{-1}}$, H_2SO_4). Instrument calibration in ICP-MS was achieved using a multi-elemental standard solution (Sn, Mg, Cu and Zn, $10\,\mathrm{\mu g\,l^{-1}}$). Serial dilutions (volume basis) of the gas standard were prepared by mixing with Ar gas in order to generate gaseous calibration standards.

Gas Injection Manifold

The manifold consisted of a gas tight syringe (30 ml), a four-way injection valve and a bubble flow meter connected by Teflon tubing. Initially gas sample was transferred into the syringe via a Teflon tube, releasing excess gas into the bubble flow meter. The sample in the syringe was then injected directly to the ICP via a sheathing gas unit (as described elsewhere) [12].

ICP-OES Instrumentation

A Spectro Analytical CIROS (Spectro Analytical, Kleeve, Germany) equipped with an axially viewed CCD based spectrometer (wavelength coverage, 120–800 nm) was used. Operating conditions for the ICP are given in Table I [9].

In operation, a 30 ml gas sample was injected manually over a period of about 60 s, the sample being pre-mixed with aerosol (via the sheathing gas unit) from conventional pneumatic nebulisation of high purity water (Millipore). The measurement cycle consisted of signal integration for 30 s, i.e., simultaneous acquisition of emission intensities for the wavelength range 120–800 nm.

ICP-MS Instrumentation

An Agilent 4500 ICP-mass spectrometer (Agilent Technologies, Cheshire, UK) was used. Gaseous sample introduction was achieved using the same gas manifold as p described for ICP-OES with the sheathing gas unit being inserted between the torch and the spray chamber. As before, high purity water was continuously sprayed into the plasma at a flow rate of 0.6 ml min^{-1}. Main operating conditions for ICP-MS are given in Table II. Ion time response for ^{118}Sn, ^{24}Mg, ^{63}Cu and ^{66}Zn were monitored for direct injection of landfill gas samples and for nebulisation of a multi-element standard solution (10 μg l^{-1}). The full mass spectrum was recorded for several landfill gas samples.

TABLE I ICP-ES operating parameters

Power (W)	1500
Nebuliser	"Cross-flow" (Spectro)
Spray chamber	Scott double pass
Outer gas (l min^{-1})	17
Intermediate gas (l min^{-1})	0.9
Nebuliser gas (l min^{-1})	0.4
Liquid uptake (ml min^{-1})	1.7
Gas injection rate (l min^{-1})	0.03
Gas injection volume (ml)	30
Integration time (s)	30
Run time (s)	60

TABLE II ICP-MS operating parameters

Power (W)	1400
Nebuliser	Babington nebuliser
Spray chamber	Scott double pass
Spray chamber temperature (°C)	4
Outer gas (l min^{-1})	16
Intermediate gas (l min^{-1})	1.0
Nebuliser gas (l min^{-1})	1.20
Liquid uptake (ml min^{-1})	0.7
Gas injection rate (l min^{-1})	0.01
Gas injection volume (ml)	30
Integration time	0.01 s/point, 6 points/ peak
Run time (s)	110

RESULTS AND DISCUSSION

Analysis of Landfill Gas by ICP-OES

Direct injection of gas samples (standard gas and landfill gas) into the ICP resulted in a stable plasma being maintained throughout experimentation. An indication of instrumental stability at the Cl line (134.72 nm) and S line (180.73 nm) is shown in Fig. 1(A and B) for (a) the background (nebulisation of water), (b) injection of landfill gas, (c) injection of gaseous standard (C_2H_5Cl, 100 mg l^{-1}) and (d) injection

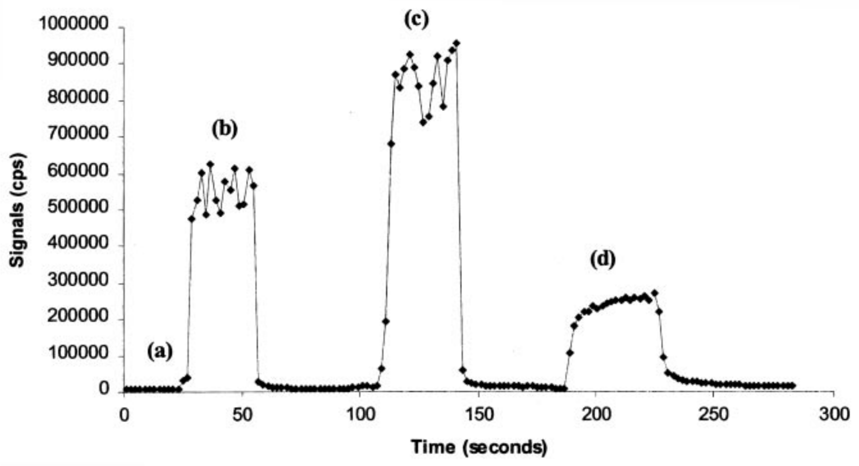

FIGURE 1A Ion-time response of chlorine (Cl 134.72 nm) for ICP-OES: (a) nebulisation of high purity water (b) injection of landfill gas (c) injection of gaseous ethyl chloride standard (C_2H_5Cl, 100 mg l^{-1}) and (d) injection of aqueous Cl standard (500 mg l^{-1}).

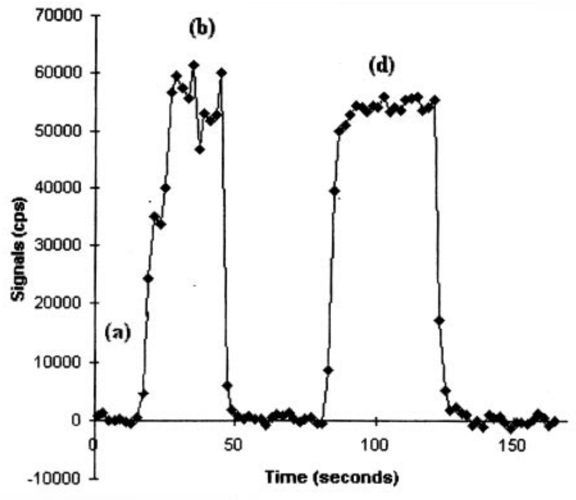

FIGURE 1B Ion-time response of sulphur (180.73 nm) for ICP-OES: (a) nebulisation of high purity water (background) (b) injection of landfill gas (d) injection of aqueous sulphur standard (20 mg l^{-1}).

of aqueous standard (Cl, 500 mg l^{-1}; S, 20 mg l^{-1}). It is evident that there is rapid wash-in and wash-out for both gaseous and liquid sample introduction routes. Further, good signal stability for the background was maintained during nebulisation of water (% RSD, 3%). For gaseous injection it can be seen (Fig. 1) that there is a degree of signal instability relative to the nebulisation of the aqueous standard solutions. That is, signal stability for Cl was 4% RSD (aqueous sample) compared to 16% RSD (gaseous standard) while the % RSD's for S were 6.5 and 18%, respectively. It is suspected that the deterioration in precision for the gas sample is related to the abrupt changes in plasma gas composition (particularly carbon content) and electrical conductivity on injection of the landfill gas.

Direct injection of landfill gas into the ICP revealed a complex UV-VIS emission spectrum (Fig. 2A). The spectrum revealed prominent chlorine (134.72, 135.17 and 135.43 nm) and sulphur (180.73 and 182.03 nm) lines and comparison with the spectra from a standard gas sample (Fig. 2B) and the argon background (Fig. 2C) suggested a relative absence of spectral interference at these wavelengths. No further elements were detected by ICP-OES suggesting lack of sensitivity or absence of trace elements in samples under the investigation. As anticipated the spectrum above 300 nm was dominated by numerous argon lines. The spectrum was initially studied with reference to spectral line library (Spectro Analytical, resident data base). However, a vast number of emission lines remained unidentified and some ambiguously assigned. As an alternate, the Atomic Spectra Data Base (ASD) produced by the National Institutes of Science and Technology (NIST) [22] was used to interpret the data. It was found that many of the emission lines recorded for landfill gas compared favourably with atomic and molecular transitions involving C, N and O. Furthermore, N and O emission lines were noted to cause spectral overlap on prominent elemental emissions (e.g. Al 176.4 nm, Cl 136.2 nm and Pb 168.2 nm).

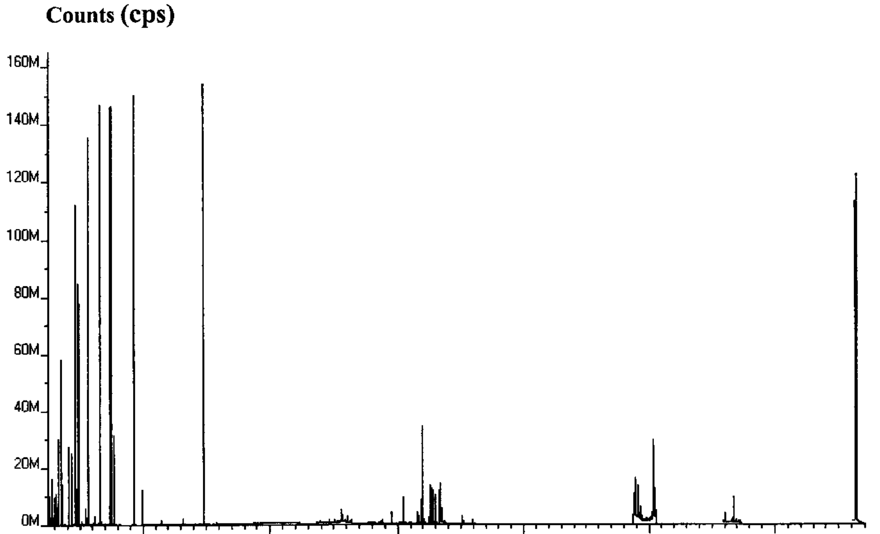

FIGURE 2A ICP emission spectra of Landfill Gas.

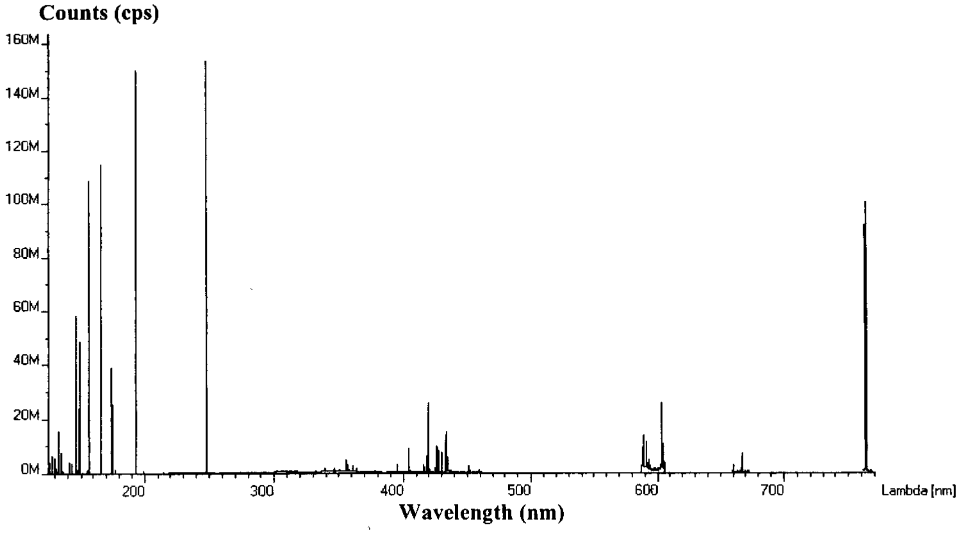

FIGURE 2B ICP emission spectra of a standard gas mixture (1000 ppm ethylene chloride in 60 : 40 mixture of $CH_4:CO_2$).

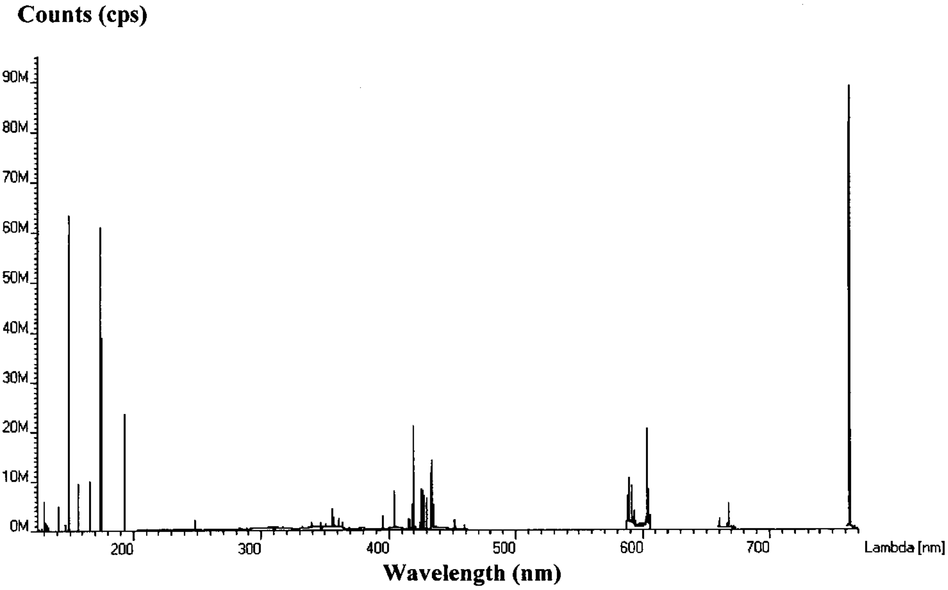

FIGURE 2C ICP emission spectra of Argon gas as a blank (Ar 99.9%).

With respect to quantitation the concentration of Cl in a landfill gas sample (Fig. 1A) was $34\,\mathrm{mg\,l^{-1}}$. This value was derived from the linear calibration data ($y = 14097x + 70537$) established for the gas standards (1 – $100\,\mathrm{mg\,l^{-1}}$ as Cl). A key aspect of this study was to provide a comparison of signal response between gaseous and liquid sample introduction routes. As shown in Fig. 1A, signal response for the gaseous route is significantly enhanced relative to liquid sample introduction (calibration equation for aqueous standards, $y = 486x + 3446$; enhancement factor for gaseous sample introduction, 39). On the assumption that 100% sample introduction efficiency is realised with gaseous injection, sample introduction efficiency in the case of aqueous standards was calculated as 2.5%. Assuming that this efficiency factor is transferable to other elements, the concentration of S in the landfill gas sample was estimated as $8.69\,\mathrm{mg\,l^{-1}}$.

Analysis of Landfill Gas by ICP Mass Spectrometry

As in the case of ICP emission spectrometry signal stability for ICP-MS was maintained during the landfill gas injection. A typical mass spectrum for landfill gas is given in Fig. 3. Given that landfill gas typically consists of 95% C based compounds (including N and O as major compounds and other trace constituents) significant interference problems were anticipated particularly for isotopes in the lower mass region ($m/z < 80$). Thus, the signal at m/z 52 was deemed to be caused by $\mathrm{ArC^+}$ and not Cr, given that Cr abundances for mass 52 and mass 53 did not equate with naturally occurring values. Examination of the mass spectrum (Fig. 3) revealed prominent signals for $^{118}\mathrm{Sn}$, $^{24}\mathrm{Mg}$, $^{63}\mathrm{Cu}$, $^{66}\mathrm{Zn}$, $^{202}\mathrm{Hg}$ and $^{208}\mathrm{Pb}$. In the case of the latter two elements ($^{202}\mathrm{Hg}$ and $^{208}\mathrm{Pb}$), however, signals were subsequently found to be due to contamination from previously analysed samples. Further investigations of $^{118}\mathrm{Sn}$ were performed as this element was found to be consistently present in landfill gas samples. Figure 4 shows a typical signal response for injection of landfill gas and an aqueous standard solution ($10\,\mathrm{\mu g\,l^{-1}}$). As in the case of ICP emission, precision was poorer in the case of the landfill gas injection, i.e. 20% RSD (gaseous) versus 3% RSD (aqueous). The concentration of Sn in the landfill gas sample was estimated to be $21.7\,\mathrm{\mu g\,l^{-1}}$ based on comparison of the respective peak height responses and assuming a similar sample introduction efficiency as for ICP emission measurement, i.e. 2.5%.

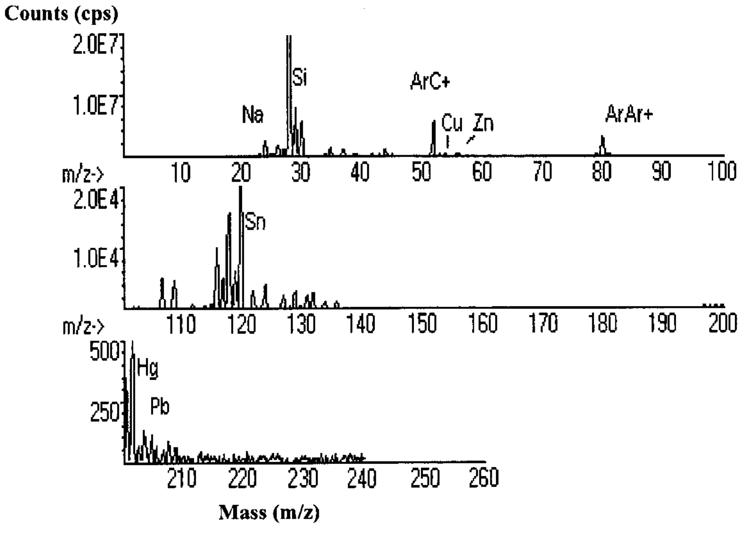

FIGURE 3 Mass spectrum (ICP-MS) of landfill gas sample. (see text for experimental details).

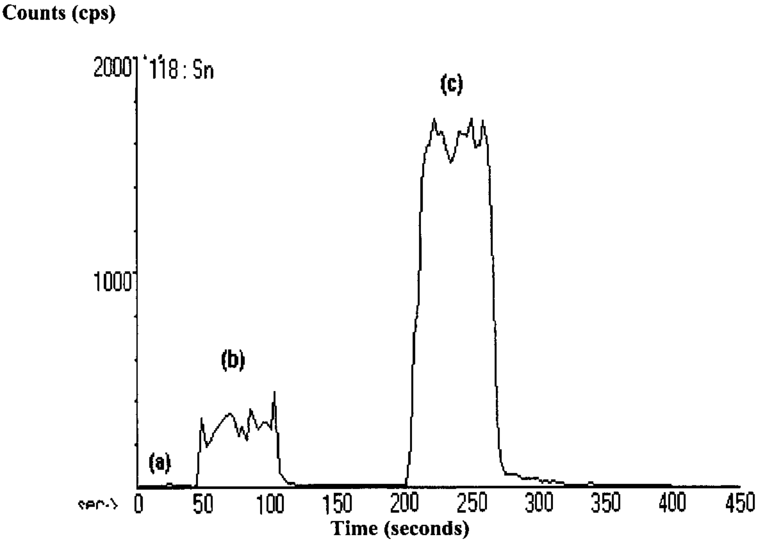

FIGURE 4 Ion time response of ^{118}Sn for ICP-MS analysis: (a) background (nebulisation of high purity water) (b) injection of landfill gas (c) injection of multi-element standard (Sn, 10 μg l^{-1}).

CONCLUSION

This direct determination of trace elements in landfill gas by ICP-OES/MS has met with some success. The ICP techniques proved to be robust and, although susceptible to spectral interference effects, were suited to the monitoring of environmentally important elements, i.e. S, Cl, Sn, Cu and Zn. Moreover it was shown, for the first time, that aqueous standard solutions can provide an important new route for quantitation, this having great significance given the relative scarcity of commercially available gaseous standards. A major concern with current trace analytical methods for landfill gas, however, relates to the reliability and integrity of sampling, sample storage and sample stability. In this work and in many others, few studies have demonstrated that analyte concentrations established for laboratory-based analysis are equivalent, or similar, to the *in situ* landfill gas composition. In future work it is proposed to investigate this aspect by utilising on-line ICP measurements with special reference to S and Cl determinations. This research will survey several landfill sites in order to build-up new environmental data bases.

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