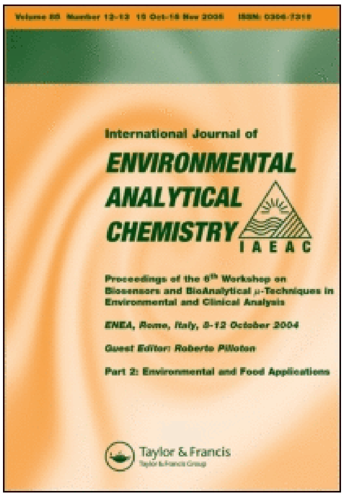

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Development of a pre-concentrator-thermo-desorber/micro-gas chromatograph/mass spectrometer coupling for on-site analyses of emissions of volatile organic compounds from landfills

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The development and use of a pre-concentrator-thermo-desorber/micro-gas chromatograph/mass spectrometer (μTD/μGC/MSD) coupling for the on-site analysis of VOCs in landfill gases are presented. The coupling has the advantage of analysing compounds with two detectors operated in series: the TCD (of the μGC) initially analyses the gas without destroying it, and then the MSD identifies the compounds. Due to the TCD response, the results were quantified with reference to toluene. The reliability of the analytical chain for quantitative analysis was validated by sampling two gaseous standards, including the EPA TO14 mixture, containing 39 compounds. With the OV1 μGC column, 24 compounds were identified and 16 correctly quantified. The repeatability of the measures estimated by their standard deviation was in the order of 1–2%. The detection limit was evaluated at 0.1 ppbv, for a 40 min pre-concentration on the Tenax of the μTD. The results of VOC analyses in the air of a landfill site obtained with the μTD/μGC/MSD coupling show its potential for on-site analyses: immediate results, high sensitivity, no storage for the samples, and measurements of pollution peaks.

Keywords: Portable μGC; Preconcentration; On-site measurements; VOC; Landfill gas

1. Introduction

A large number of volatile organic compounds (VOC) exist in air. Their emissions in the atmosphere may have a negative impact on the environment such as the formation of

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ground-level photochemical ozone, the enhancement of the global greenhouse effect, and the depletion of the stratospheric ozone. They can also cause serious health problems in the form of toxic, carcinogenic, and mutagenic effects, which may vary depending on the individual or synergistic behaviour and on the exposure conditions [1, 2].

The challenge for the analytical approach is to detect trace amounts of VOCs in complex matrices, such as biogas coming from household waste landfills, with sufficient sensitivity. Pre-concentration of VOCs on a sorbent material is therefore to be used, followed by the separation of compounds with gas chromatography after thermal desorption or solvent extraction.

A number of sorbent sampling techniques have been reported for the analysis of VOCs from landfill gases. Eitzer [3] used sorbents like Carbotrap-300 and Tenax GC with analysis by thermal desorption/GC-MS. Allen *et al.* [4] used sampling tubes containing a sandwich of three adsorbents, Tenax TA, Chromosorb 102, and Carbosieve III for the determination of trace VOCs in landfill gas using automated thermal desorption–gas chromatography–mass spectrometry. Kim and Kim [5] used a combination of Carbosieve adsorbents (Carbotrap C, Carbotrap B, and Carbosieve S-III) and detection by Perkin Elmer ATD 400/GC/FID for the measurement of VOCs in the atmosphere of an abandoned landfill site. Harper [6] realized an important review on the use of sorbents in trapping VOCs in air for subsequent analysis. Although the sorbent tube techniques can show good performances (e.g. high sensitivity for a wide range of compounds), the analyses are often performed in the laboratory, far away from the emission source and a long time after the sampling. The advantage for on-site instrumentation which allows an analysis as close as possible to the source appears to be an important issue. At present, only Davoli *et al.* [7] used a μTD/μGC (TCD) coupling for on-site analysis, the compounds being identified by retention time. Therefore, the combination with a GC-MS technique was thought to be of interest.

On-site analysis yields relevant information on the variation of the emissions' intensity in relation to time and even interesting information on industrial process performances. Implementing on-site analyses requires a reliable identification and quantification with a relatively good sensitivity, all these conditions being at first sight incompatible with the requirement of a short analysis time (10–15 min).

The development of transportable instrumentation was carried out keeping as much as possible: limited operating costs, high sensitivity, possibility of the acquisition in SCAN and SIM modes, important mass scan range, fast identification from a computer library and short time of analysis in order to use the results on site.

There are other GC/MS couplings that can be used on site (portable HAPSITE GC/MS, Bruker EM 640S Transportable GC/MS System, etc.) but none with the TCD and MSD double detection present in our coupling, which has been used for the environmental analyses of emissions of volatile organic compounds from landfills.

2. Experimental

The analysis of gaseous samples was carried out using the portable micro-chromatograph P200H from Agilent Technologies, which has a detector with a good sensitivity in direct analysis (about 10 ppm) for an analysis time not exceeding 160 s.

Separations were performed on an OV1 column (8 m × 0.1 mm i.d., 1 μm film thickness).

The P200H chromatograph does not have temperature programming, and in this case, preliminary measurements were undertaken in laboratory to set the optimal temperature. Different column temperatures were tested: 40, 80, 130, and 160°C. For on-site analyses, the 80 and 130°C temperatures were found to be the most appropriate for the studied mixtures. The μGC sampling time was 10 s, and the injection time 200 ms; the head column pressure was fixed at 27.3 psi. Helium was used as the carrier gas.

The μGC was equipped with a micro-thermal conductivity detector (μ-TCD), which has the advantage of providing a linear response in all the concentration range with an intensity response rather similar for each organic compound [8]. The TCD chromatograms were exploited with the EZChrom 200 Data System software, version 4.5.

Because of low concentration measurements, a step of pre-concentration was needed. This was achieved by an Airsense EDU 2 pre-concentrator-thermo-desorber (μTD) connected to the μGC. The μTD manages the phases of enrichment on sorbent, the thermal desorption and the transfer into the μGC. Tenax TA (SKC # 35.03) was used as the sorbent material. The operational conditions of μTD were finalized after validation in the laboratory and on site.

The parameters programmed in the AIRSENSE software were: a sampling temperature of 45°C; a sampling time varying in relation to the targeted objective from 30 s (to measure air concentrations in the order of ppm) up to approximately half an hour (to detect lower concentrations, in the order of ppb); a desorption of the compounds at 250°C during 160 s; an injection time of 16 s; an injection temperature of 250°C; and a sampling flow rate of 100 mL min^{-1}.

A mass selective detector MSD Agilent Technologies 5973 was coupled to the μGC by means of a patented interface [9, 10]. The MSD software is ChemStation, revision D.00.01. The mass spectrometer was used in the m/z range of 19–300, and the interface was designed to ensure the quasi-complete transfer of the flux leaving the TCD of the μGC to the MSD. The performances of identification of the separated compounds depend on their quasi-complete (>99%) transfer to MSD. The MSD response depends on the quantity of detected compound [8]. The TCD and the MSD were operated in series, so two chromatograms were obtained.

For the validation of the analytical method, two standard mixtures were used: one from Praxair and the EPA T014 standard, purchased from Supelco. Their compositions are shown in table 1. After the optimization of the coupling with the standard mixture Praxair, all other tests were carried out with the more complete standard mixture EPA TO14.

The analyses were carried out on two different sites (*A* and *B*), both being representative of the majority of modern municipal waste landfills in France and similar in both methods of operation and construction to those in other industrialized countries. None of the sites were licensed to accept toxic or industrial waste. The experimental conditions were:

- Site A: analysis of gaseous emissions from a municipal waste cell in use after aspiration in Tedlar bags during 45 s with a membrane pump KNF N 820 FT-18 fitted with an internal Teflon coating to avoid VOC adsorption.

- Site B: analysis of gaseous emissions from a flux box used to measure the flux of the VOCs emitted at the surface of a clay cover of a closed municipal waste cell. In this case, the Tedlar bag was filled with the gas mixture by depression in a box.

Table 1. Composition of the Praxair and EPA TO14 standard gas mixtures.

Compound	C (mg N m^{-3})
Praxair[a]	
Ethanol	4.97
Vinyl chloride	5.02
n-Pentane	19.0
Dichloromethane	4.67
n-Hexane	20.6
Toluene	4.70
n-Heptane	4.89
n-Octane	5.75
Dichlorodifluoromethane	5.00
EPA TO14[b]	
Methyl chloride	2.48
Vinyl chloride	2.98
Ethyl chloride	3.08
Benzene	3.66
Methylene chloride	4.09
Toluene	4.32
Bromomethane	4.36
1,1-Dichloroethene	4.76
cis-1,2-Dichloroethylene	4.50
1,1-Dichloroethane	4.64
1,2-Dichloroethane	4.59
Ethylbenzene	4.88
m-Xylene	4.88
p-Xylene	4.93
o-Xylene	4.88
1,3-Dichloro-1-propene (E)	4.60
1,3-Dichloro-1-propene (Z)	4.87
Styrene	4.81
Chlorobenzene	5.18
1,2-Dichloropropane	5.30
Chloroform	5.60
1,2,4-Trimethylbenzene	5.42
1,3,5-Trimethylbenzene	5.47
Dichlorodifluoromethane	5.72
Trichloroethylene	6.16
1,1,1-Trichloroethane	6.31
1,1,2-Trichloroethane	6.13
Trichloromonofluoromethane	6.62
1,2-Dichlorobenzene	6.49
1,3-Dichlorobenzene	6.56
1,4-Dichlorobenzene	6.56
Carbon tetrachloride	7.48
Tetrachloroethylene	8.00
1,1,2,2-Tetrachloroethane	7.80
Tetrafluorodichloroethane	8.16
1,2,4-Trichlorobenzene	7.60
1,1,2-Trichloro-1,2,2-trifluoroethane	8.70
1,2-Dibromoethane	8.29
Hexachloro-1,3-butadiene	11.02

[a] Mixture prepared in nitrogen; the uncertainties are 1% for all concentrations around 5 mg N m^{-3} and 0.5% for all concentrations around 20 mg N m^{-3}.
[b] Mixture prepared in nitrogen; the concentrations are given with an uncertainty of 10%.

For all validation tests and on-site analyses, the gaseous samples were collected in a Tedlar bag as an intermediary between the source of compounds and the μTD/μGC/MSD coupling. The samples were quickly trapped on the Tenax of the μTD to avoid adsorption of compounds during their storage and then analysed with the μGC/MSD coupling.

3. Results and discussion

3.1 *Validation of the µTD/µGC/MSD coupling*

Validation for the qualitative analysis was not necessary because of the reliability of the compounds identification with the MSD. The mass spectra obtained were directly exploited by software comparison with the NIST mass spectra database [11]. However, in a few particular cases (some isomers, e.g. *para*- and *ortho*-xylenes), a complementary identification based on retention times may be necessary.

The accuracy of a quantitative analysis depends on two stages preceding the injection onto the μGC column: the enrichment on Tenax and its thermal desorption. The output of fixation and thermal desorption could be different from unity when breakthrough volumes are reached or if competition for adsorption occurs. The experimental conditions must therefore be carefully determined to minimize these drawbacks:

- the sorption time has to be short for concentrated samples;
- the sorption flow has to be carefully chosen depending on the nature of the compounds and their concentration [12].

Figure 1 provides the first elements of response acquired with the standard mixture Praxair, which contains only non-polar compounds.

Figure 2(a) and (b) show the response of the coupling for the compounds sampled above the surface of a municipal solid waste pilot landfill. This analysis permitted the testing of the response of the coupling for the volatile polar compounds present in the sample.

Except for 2-butanone, which is present in high concentrations (the breakthrough volume was reached for this compound), the TCD response increases linearly in relation

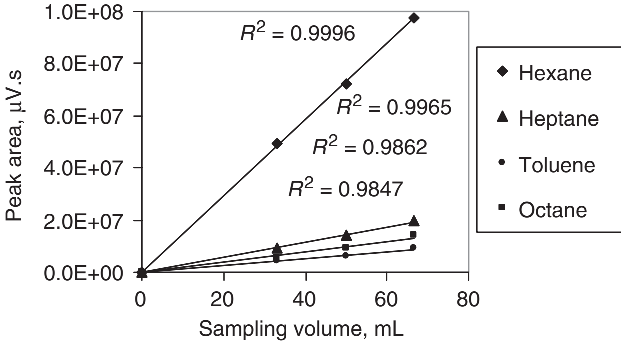

Figure 1. Variation of the TCD peak area according to the sampling volume on Tenax TA (sampling flow rate: 100 mL min^{-1}; column temperature: 80°C) for the standard mixture Praxair.

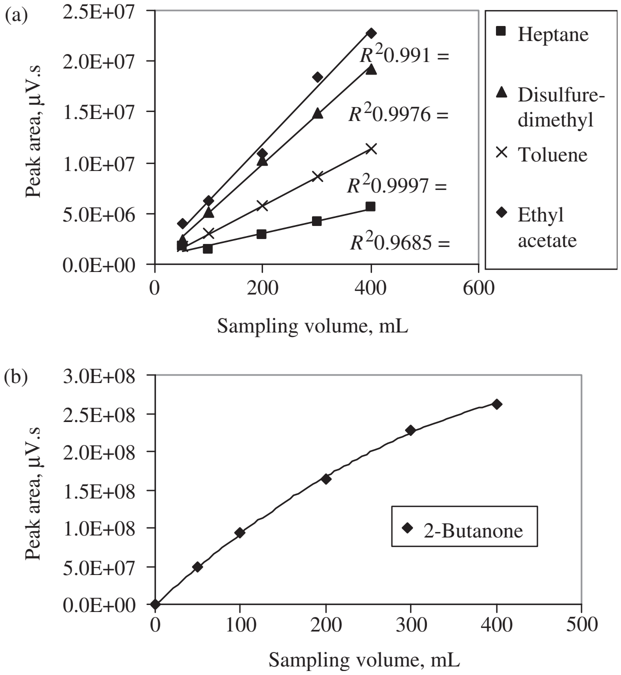

Figure 2. (a, b) Variation of TCD peak area according to the sampling volume on Tenax TA (sampling flow: 100 mL min^{-1}; column temperature: 80°C) for a gas mixture sampled at the surface of a municipal solid-waste pilot landfill.

to the volume of gas which has gone through the Tenax tube during the enrichment phase. The linearity of the response allows us to consider using this coupling in a quantitative analysis. This can be achieved with a prior calibration which has to be made frequently because the adsorption capacities of the Tenax of the pre-concentrator μTD may vary over a period of time depending on the ageing of the adsorbent material. Therefore, during the period of analyses, the system had to be calibrated every day.

The quantitative analysis of very complex mixtures, covering a wide range of concentrations, could be seriously affected by the adsorption competition of compounds on Tenax. To evaluate the influence of this competition, the Praxair and EPA TO14 mixtures, both containing toluene, were analysed the same day. A 30 s sampling time (or 50 mL sampling volume) was chosen for the two studied mixtures. The values obtained with the TCD detector are presented in table 2.

The response factor of toluene was calculated for the two standard mixtures. The observed difference was calculated as a standard deviation and was found to be in the order of 12.9%, which can be explained by the concentration uncertainties of about 10% given by the manufacturer for the standard mixture EPA TO14 and by the competition phenomena during the toluene adsorption. This value can be considered as satisfactory if we take into account the uncertainty of about 15% given by ASTM [13] for all the analytical chain, starting with the sampling by pre-concentration on sorbent tubes and ending with the GC-MS analysis. The μTD/μGC/MSD coupling can therefore be used for a quantitative screening on site, and toluene was chosen as the reference compound.

Table 2. TCD response of toluene in two standard gas mixtures.

Standard gas mixture	Compound	Concentration (μg N m^{-3})	Area (μV.s)	K (μg N m^{-3} μV^{-1} s^{-1})
Praxair	Toluene	4700	9 807 340	4.79×10^{-4}
EPA TO14	Toluene	4320	10 256 008	4.21×10^{-4}

Rigorous quantitative results need a calibration of coupling for every compound, but this calibration technique is time-consuming and not justified in a first approach. Furthermore, the quantitative response of the TCD theoretically depends little on the analysed organic compound [8], which makes the quantification with reference to a compound reliable. On the other hand, it is obvious that the MSD detector gives better results when the calibration can be carried out for every compound.

After a first validation of the analytical chain, the analysis of the environmental standard mixture EPA TO14 was performed under the same conditions that were to be used on-site: a Tedlar bag was filled with the gas mixture and immediately analysed by μTD/μGC/MSD coupling, with a sampling time of 30 s (or 50 mL sampling volume) and a μGC column temperature of 80°C and 130°C, respectively. The TCD and the MSD chromatograms obtained at a μGC column temperature of 80°C are presented in figure 3.

The results of the EPA T014 standard gas mixture obtained with the μTD/μGC/MSD coupling are shown in table 3. By comparing the real concentrations of the compounds in the standard mixture TO14 with the concentrations calculated with reference to toluene (table 3), it can be observed that the quantitative value of the TCD is closer to that expected than the MSD response.

The analysis at 80°C allowed the detection of 17 VOCs (using TCD); 12 of these exhibited concentrations with differences 12% lower than those of the real values. With the MSD, only five VOCs could be identified and quantified with the same precision. Taking into account the uncertainty of 10% for the compounds concentrations in the standard gas mixture TO14, a confidence interval of 12% was retained.

The results obtained at a column temperature of 130°C were less precise. Table 3 shows that for the TCD, only four VOCs were quantified with values less than 12% different from their real values and only toluene for the MSD, because of the low resolution at this temperature. Also, at 130°C, the peaks with low retention times (RT < 36 s) show co-elution. However, these compounds (1,2-dichloroethene, chloroform, 1,2-dichlorethane, 1,1,1-trichlorethane, benzene, and trichloroethylene) are correctly separated at 80°C. We would therefore favour the quantitative TCD results obtained from the analysis at 130°C only for the compounds specifically detected at this temperature.

Two contrasting temperatures (40 and 160°C) were then tested in order to detect the low and heavy compounds. At 40°C, the trail of the air peak partly hides the VOCs, whereas at 160°C the heavy compounds are certainly detected, but co-elutions multiply. In turn, the analysis at 40°C makes it possible to observe compounds, different from those identified at 80°C: 1,1-dicloroethene, 1,1,2-trichloro-1,2,2-trifluoroethane and (*Z*)-1,2-dichloroethene, and at 160°C the peak of 1,2-dichlorobenzene, not identified at 130°C, was observed.

The two chosen temperatures, 80°C and 130°C, are well adapted to separate the compounds of the standard gas mixture, since 24 compounds were identified, and

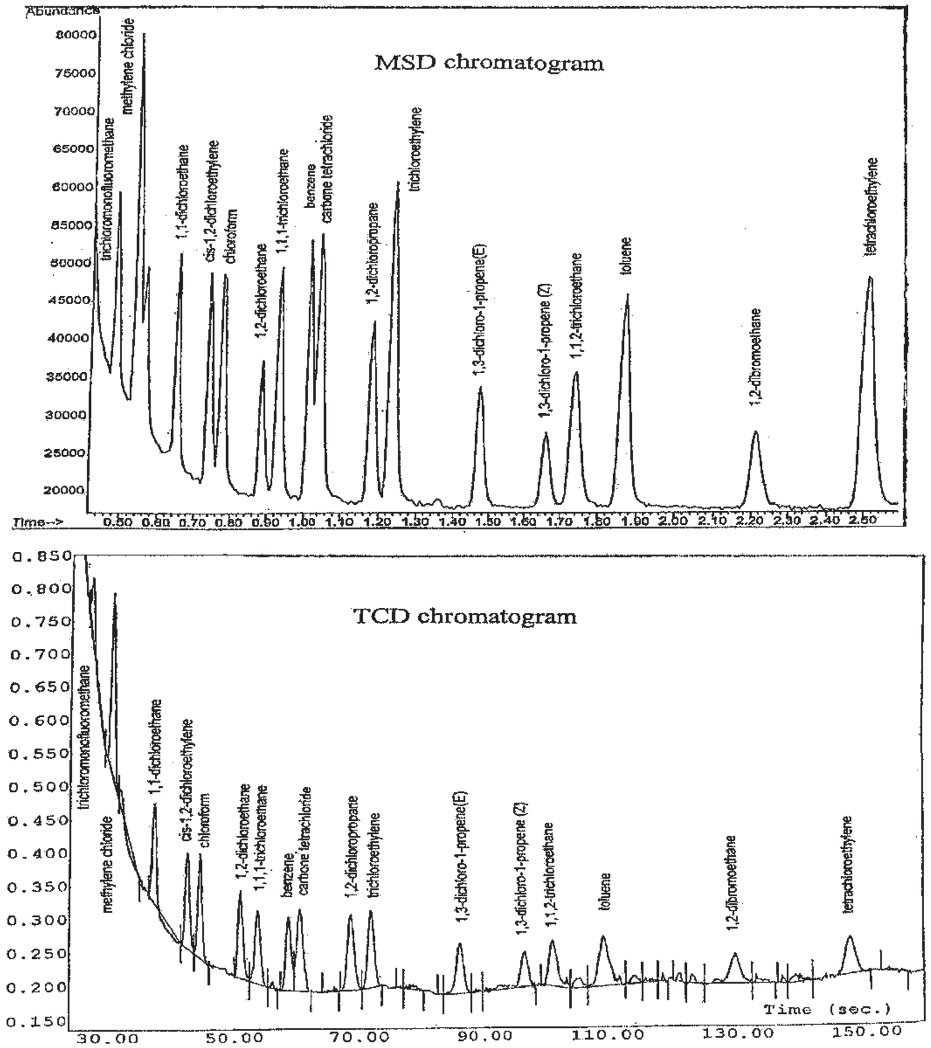

Figure 3. TCD and MSD (TIC) chromatograms of EPA TO14 standard gas mixture at a μGC column temperature of 80°C.

the resolution was sufficient to enable the quantification. The possible explanations for the identification of only 24 compounds out of 39 are: (1) the elution of light compounds in the trail of the air peak; (2) the non-retention of very light compounds on Tenax of μTD because of the high sampling temperature (45°C); and (3) the non-detection of heavy compounds at 80 and 130°C column temperatures.

Obviously, a μGC with column oven temperature programming would have been useful to avoid co-elution problems and to obtain results with only one analysis instead of two (at 80 and 130°C). Another solution to improve the detection of light and heavy compounds would be to install on the μGC the complementary OV1 columns with different lengths: longer (12 or 15 m length) for light compounds and shorter

Table 3. Analysis of the standard mixture EPA TO14 at 80°C and 130°C µGC column temperatures.

Compound (concentrations in standard mixture EPA TO14, mg N m^{-3})	RT$_{TCD}$ (s)[a]	C$^{b}_{TCD}$ (mg N m^{-3})	RT$_{MSD}$ (s)[a]	C$^{b}_{MSD}$ (mg N m^{-3})
80°C				
Trichloromonofluoromethane (6.62)	26.8	1.45	28.2	7.56
Methylene chloride (4.09)	30.3	7.82	31.8	11.90
1,1-Dichloroethane (4.64)	36.9	4.95	38.4	5.13
cis-1,2-Dichloroethylene (4.50)	42.3	4.27	43.8	3.18
Chloroform (5.6)	44.4	4.95	45.6	4.93
1,2-Dichloroethane (4.59)	50.8	4.12	52.2	3.45
1,1,1-Trichloroethane (6.31)	53.6	5.60	55.2	4.41
Benzene (3.66)	58.6	4.08	60.0	3.89
Carbon tetrachloride (7.48)	60.4	6.59	61.8	5.09
1,2-Dichloropropane (5.30)	68.4	4.78	70.2	3.14
Trichloroethylene (6.16)	71.6	5.43	73.2	5.65
1,3-Dichloro-1-propene (E) (4.60)	85.6	4.05	87.6	2.11
1,3-Dichloro-1-propene (Z) (4.87)	96.4	2.23	98.4	1.35
1,1,2-Trichloroethane (6.13)	101.1	5.41	103.2	3.17
Toluene (4.32)	109.1	4.32	111.0	4.32
1,2-Dibromoethane (8.29)	129.2	2.65	131.4	2.09
Tetrachloroethylene (8.00)	147.3	4.39	149.4	5.77
130°C				
1,3-Dichloro-1-propene(E) (4.60)	39.7	4.62	41.4	2.48
1,3-Dichloro-1-propene (Z) (4.87)	42.2	3.27	44.0	2.21
1,1,2-trichloroethane (6.13)	43.9	5.40	45.7	1.72
Toluene (4.32)	46.2	4.32	48.0	4.32
1,2-Dibromoethane (8.29)	52.1	3.42	54.6	1.89
Tetrachloroethylene (8.00)	55.8	5.86	57.6	3.08
Chlorobenzene (5.18)	63.3	2.93	66.0	0.96
Ethylbenzene (4.88)	67.5	3.75	70.2	1.45
m-Xylene (4.88)	69.9	3.65	72.6	2.38
p-Xylene (4.93)	75.9	1.71	78.7	0.93
o-Xylene (4.88)	77.9	4.70	81.0	4.73
1,2,4-Trimethylbenzene (5.42)	110.1	1.95	115.2	2.26
1,3,5-Trimethylbenzene (5.47)	147.3	1.83	131.4	2.51

[a] RT: retention time.

[b] Concentrations are expressed with reference to toluene.

(4 m length) for heavy compounds. In this case, the analysis can be made simultaneously on all columns, which implies only one sampling, but the coupling with the MSD can be made only on one column.

Due to the high sampling temperature (45°C) on Tenax, the detection of highly volatile compounds is only qualitative. The technical solution would probably be to lower the temperature of Tenax during the adsorption phase. A decrease in temperature down to −20°C would improve the adsorption of light compounds such as vinyl chloride [14] and therefore allow for the analysis of all light compounds present in the EPA TO14 standard gas mixture. In this case, the removal of the air peak from the μGC chromatogram by passing helium gas on Tenax of the pre-concentrator would allow analysis of the highly volatile compounds.

The standard Praxair and TO14 mixtures were used for the implementation and validation of the μTD/μGC/MSD coupling. The same standard mixtures were used for the quantitative calibration of the coupling when the on-site analyses were performed. For the compounds which were not present in the standard mixtures, further calibrations were realized by injection of the pure compound in the Tedlar bag, which was then filled with nitrogen.

To estimate the repeatability of the measures, many tests were realized with the standard mixture Praxair. The standard deviation was calculated and found to be in the order of 1–2% for the detected compounds.

3.2 *On-site analyses with the μTD/μGC/MSD coupling*

3.2.1 Landfill cell side analyses. Two measurements were carried out in the atmosphere of a French municipal solid waste landfill (site A): two Tedlar bags were filled at 5 min intervals, one on a non-active waste cell side (bag 1), the other (bag 2) in a zone with an intense activity also called the 'active cell' (trucks discharging fresh waste, engines compacting and laying out fresh waste, etc.), both of them 2 m above the waste surface.

The results obtained (table 4) show that the number of compounds and their concentrations are higher in the area of the active cell (bag 2). Disturbing waste creates new surfaces and exposes old surfaces from which volatiles can evaporate [15, 16].

Table 4. On-site analyses of the atmosphere of a municipal solid- waste landfill performed with the μTD/μGC/MSD coupling at two different μGC column temperatures.

Compound/concentration (μg N m^{-3})	Column temperature of μGC, 80°C		Column temperature of μGC, 130°C[a]	
Sample volume	Bag 1[b] (3 L)	Bag 2[c] (4 L)	Bag 1[b] (2 L)	Bag 2[c] (3 L)
Methylene chloride		3.9		
2-Butanone	2.9[d]	75.9[d]		
Ethyl acetate	11.8[d]	91.4[d]		
1,2-Dichloroethane		4.4		
1-Butanol	14.7[d]	4900.6[d]		
Benzene	23.4	40.1		
Cyclohexane	5.9[d]	13.3[d]		
Trichloroethylene	40.4	71.6		
Heptane	6.2	63.4		
Methyl isobutyl ketone	20.9[d]	263.2[d]		
1,1,2-Trichloroethane	1.7	17.8		
Toluene	83.5	1032.4		
Butyl acetate	59.9[e]	1456.6[e]		
Octane	10.5	120.2		
Tetrachloroethylene	9	47.1		
Ethylbenzene			35.8	509.2
m-Xylene			46.5	759.1
o-Xylene			2.3	90.9
Nonane			40.9[d]	522.7[d]
α-Pinene			4.4[d]	42.6[d]
1,3,5-Trimethylbenzene			34.1	364.5
Limonene			197.6[e]	415.7[e]

[a] At 130°C, only the compounds identified at this temperature are given.

[b] Bag filled in the non-active waste cell side.

[c] Bag filled in the active waste cell side.

[d] Concentrations are given in reference to toluene, because these compounds are not present in the Praxair and EPA TO14 standard mixtures.

[e] For butyl acetate and limonene, a calibration was carried out by syringe injection of the pure compound in a Tedlar bag.

Higher concentrations are observed in bag 2, for 1-butanol (330 times higher than in the bag 1), but also for toluene and butyl acetate.

The content of each bag was analysed at two temperatures, 80 and 130°C, in order to detect a wide range of compounds. A qualitative analysis was carried out at a μGC column temperature of 40°C, and the identified compounds were: *n*-butane, chloroethane, and trichloromonofluoromethane; other compounds like methylene chloride, ethyl acetate, 1-butanol, and cyclohexane were also identified at 80°C.

The aim of the comparison between the two areas (active cell and non-active cell) was to show the large influence of lorries unloading waste and of the compacting engines on air pollution.

Pollution peaks (high concentrations obtained in a very short time; the Tedlar bag was filled with the gas sample in 45 s) were observed for several compounds like 1-butanol, toluene, and butyl acetate, and it is very likely that the breakthrough volume was reached for them. The concentration obtained for these compounds is then a minimal value, but the information is sufficient to focus attention on pollution (caused by lorries unloading waste) and its nature. The pre-concentrator conception does not allow the assembly of a second sorbent tube in series to check the breakthrough volume for these compounds. In this case, to avoid the breakthrough phenomena, a small sampling time can be used (in our case, the sampling time on Tenax was 40 min, because we wanted to detect all the present compounds, in particular those present in low concentrations).

3.2.2 Landfill cell clay cover analyses. The coupling was also used on site to measure the diluted gas mixtures, at the output of a flux box, coming from municipal waste closed cells (site B).

The aim of this type of analysis was to evaluate the permeability of a landfill cell clay cover and to check that there was no gaseous leak. A flux box was used to determine the fluxes of gaseous compounds emitted by a solid surface. The flux box was swept by a nitrogen flux (parallel with the emission surface of $0.1134\,\mathrm{m}^2$) of $6.7\,\mathrm{L\,min}^{-1}$, meaning that the sample was highly diluted, and in this case, the concentrations of the emitted compounds were very low. This is why the volume of sampled gas for pre-concentration was high (3.5 L).

Two compounds, methyl cyclohexane and dimethyl sulphide, identified by MSD, were found at very low concentrations (0.20 and 0.11 ppbv, respectively expressed with reference to toluene) using the TCD chromatogram at 80°C (figure 4). These values, obtained with a pre-concentration time of 40 min, indicate a detection limit for the μTD/μGC/MSD coupling of approximately 0.1 ppbv (twice the background noise value of the TCD chromatogram), which seems to be an acceptable limit for the identification and evaluation of concentrations of trace compounds within a reasonable time of analysis.

4. Conclusion

The development of the μTD/μGC/MSD coupling, the results of all the validation tests, and the on-site measurements allow us to outline the advantages of on-site

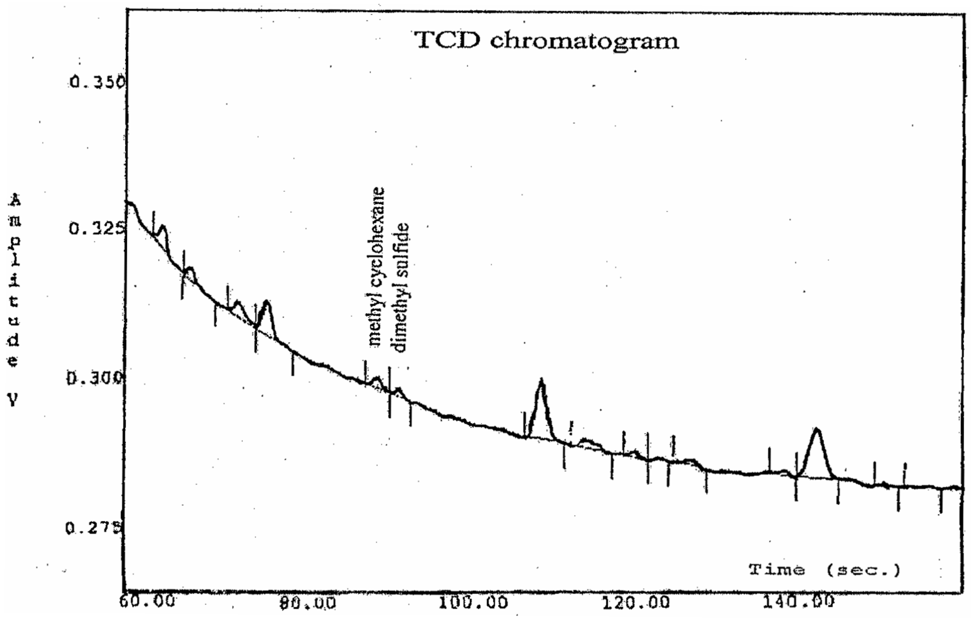

Figure 4. TCD chromatogram of a diluted gas mixture sampled at the surface of a landfill cell clay cover by means of a flux box.

measurements against laboratory measurements:

- The coupling can be used in a large domain of concentrations, provided that successive analyses are carried out (especially for unknown samples) on the same sample following: (1) without a pre-concentrator; (2) with a low pre-concentration time; (3) with a high pre-concentration time (up to 40 min), with adaptation of the sampling time depending on the preceding analyses, which necessitates the use of a Tedlar bag for sampling.
- The results of on-site analyses obtained with the μTD/μGC/MSD coupling are important to define the pre-concentration times for sampling on sorbent tubes (charcoal, Tenax, etc.) which are generally carried out 'blindly' on site, since the laboratory analyses are carried out after the sampling.
- Another advantage is the rapidity of the response. For concentrations of about 1 ppm, results are obtained in less than 15 min, and for low concentrations of about 0.10 ppb, results are obtained in 35–40 min.

An evaluation of the results shows that 24 VOC of 39 present in the EPA TO14 mixture were identified and quantified at 80 and 130°C. At the current state of development, the coupling is unable to avoid co-elution problems and to detect very light compounds, but experiments are in progress to improve performances (a μGC with column oven temperature programming; a decrease in the sampling temperature on the Tenax, etc.).

The number of VOCs present in a landfill site is generally much higher than 100 [17], and only BTEX, styrene, chloro-benzene, and dichloro-benzene can be quantified by this coupling with the standard mixture EPA TO14. In this case a quantitative analysis cannot be carried out with a calibration for every product, but only with quantification in reference to a selected compound. The studied coupling is the only one that exists to date with a double detection: a MSD for identification and a TCD which is better adapted for the expression of quantitative results in reference to a compound. The results of VOC analyses in the atmosphere of a landfill site show the potential of μTD/μGC/MSD coupling for all the qualitative and quantitative analyses: immediate results (less than 15 min for concentrations around 1 ppmv), a low detection limit of about 0.1 ppbv, no storage for the samples, and measurements of pollution peaks.

The analytical technique described here can be used in other applications, as in the study of air emissions from household waste landfills, the monitoring of emissions from industrial processes, the kinetic evaluation of atmospheric reactions, etc.

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