

# Determination of volatile organic compounds in coal, fly ash and slag samples by direct thermal desorption/GC/MS

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**Abstract.** This work proposes a method for quantifying volatile organic compounds (VOCs) in coal, fly ash and slag, coming from coal-fired power stations, using direct thermal desorption coupled with gas chromatography (GC) and mass spectrometry (MS) detection. The described method requires practically no sample handling and is precise and sensitive. Aromatic and aliphatic hydrocarbons (benzene, toluene, alkylbenzenes, heptane and octane) are the most abundant compounds in these solid samples, coal samples presenting higher levels than fly ash and slag. Other compounds (acids, ketones, aldehydes, limonene, etc.) were identified by mass spectrometry.

**Keywords.** Thermal desorption – volatile organic compounds – coal – fly ash – slag – GC-MS.

## Introduction

Volatile Organic Compounds (VOCs) have received much scrutiny from the regulatory community because many of these compounds are toxic/mutagenic and also participate in the photochemical reactions that lead to smog formation. Power generation is an important anthropogenic source due to the great volume of emissions produced, however, available data on emission of volatile organic compounds (VOCs) by power stations are incomplete [1].

Coal has a significant amount of organic matter in its structure which can be transformed during combustion processes in power generation. To understand these transformations, gaseous emissions [2] and compounds trapped in fly ash and slag must be analysed.

The analysis of organic matter content in solid samples has usually been carried out by gas chromatography (GC) or GC-mass spectrometry after extraction and concentration with rotary evaporation or nitrogen stream [3,4]. However, for VOCs determination, these techniques are not adequate. VOCs are likely to be lost through the processes of evaporative concentration, and for compounds having boiling points similar to those of solvents, solvent extraction cannot be applied.

Several authors have used thermal desorption techniques coupled with concentration to low temperature (–10 to –150°C) systems and gas chromatography for analysis of solid samples: soil, plants, wood, etc. [5-9]. Garcia *et al.* [1] and Bofanti *et al.* [10] present a thermal and pyrolytic methods to determine organic compounds trapped in coal.

This work proposes a rapid, precise and sensitive method to quantify 23 volatile organic compounds in coals, fly ash and slag based on thermal desorption/GC/MS. Mass spectrometry allows to obtain important qualitative information about samples.

## Experimental

### Sample characteristics

In this work five (A-E) types of coals, coming from a coal-fired power station feed, were analysed. VOC levels trapped in fly ash and slag, generated in coal combustion, were also determined. A maximum of six samples was taken during a one year sampling campaign.

Coal A is a subbituminous South African coal with a high carbon content (70 %) and low sulphur content (< 1 %). Coal B is a bituminous Spanish coal with similar characteristics to A (% Carbon = 60 %; % Sulphur = 1 %). C is a mixture of subbituminous coal and poor black lignite, presenting 40 % carbon and 3 % sulphur. D is a mixture of black lignite and limestone used as Fluidised Bed Power Station feed. This mixture contains 27 % carbon and 1.5 % sulphur. Lastly, coal E has low carbon content (43 %) and high sulphur content (3.5 %).

### Thermal desorption conditions

The Perkin-Elmer ATD-400 automatic thermal desorption system was used in this work for direct thermal desorption of solid samples (coal, fly ash and slag). An amount of 6-8 mg of coal was placed in empty desorption tubes plugged

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at both ends with silanised glass wool. A 60-70 mg sample of fly ash or slag was placed into the tubes.

The desorption tubes containing coal samples were heated to 350 °C for 5 minutes. Higher temperatures did not produce an improvement on VOC response. The volatile compounds were desorbed with a stream of ultrapure helium at 100 ml/min and collected in a cold trap (-30 °C) packed with 20 mg of Tenax-TA. The trap was heated quickly to 300 °C and analytes transferred to a chromatographic column, with a split division through a capillary transfer line heated to 200 °C. Different amounts of sample (10-50 mg) and different split ratios (1:3-1:10 mL/min) were tested, but worse results were obtained with high masses and split ratios due to big peak broadening, not enough sensitivity or saturation in the detector. The same desorption method was employed for fly ash and slag. Only the split division was changed to 1:3 ratio.

### Chromatographic conditions

The GC system consists of a Perkin-Elmer AutoSystem gas chromatograph with a fused silica capillary column with 5 % diphenyl and 95 % dimethyl polysiloxane (Sugelabor, 50 m × 0.25 mm × 0.25 μm film thickness). Chromatographic conditions were as follows: the column temperature is kept at 40 °C for 5 min, then increased at 5 °C/min to 160 °C, kept at this temperature for 1 min, and increased at 10 °C/min to 210 °C. Helium flow rate was 0.9 mL/min.

### Mass spectrometry conditions

Compounds are detected by a Perkin-Elmer Q-Mass 910 mass spectrometry scanning in a mass range of  $m/z = 35$  to 350. Analytes are identified by mass spectra. Calibration plot construction and sample quantitation are achieved using the external calibration method; the value of the total ion current was not used. To improve the signal/noise ratio and the resolution of poorly separated peaks the areas of the most abundant ions in each mass spectrum are used. When GC/MS was used, it was possible to work in either SCAN mode (scanning a range of selected masses) or SIM mode (Selected Ion Monitoring) where only the ions of interest are registered. Although the latter mode is more specific and provides more sensitivity, in this work SCAN mode was used because it provides sensitive enough detection and more exhaustive sample information. For quantitation, liquid standard mixtures of analytes were employed spiking 1 μL into the desorption tubes packed with 200 mg of Carbotrap b, an adsorbent commonly used to trap volatile organic compounds.

## Results and discussion

### Sensitivity of detector

Limits of detection for solid samples are shown in table I. The limits of detection obtained were similar to those

**Table I.** Limits of detection for the proposed method (ng/g).

	Coal	Fly ash and slag
1,2-Dichloroethane	532	151
Benzene	13	3.58
Heptane	6	1.79
Bromodichloromethane	257	73.3
Toluene	31	8.94
1,1,2-Trichloroethane	75	21.4
Dibromochloromethane	225	64.3
Octane	63	17.9
Tetrachloroethene	56	16.1
Ethylbenzene	25	7.15
m+p-Xylene	13	3.58
Styrene	63	17.9
o-Xylene	13	3.58
1,1,2,2-Tetrachloroethane	194	55.4
Isopropylbenzene	19	5.36
n-Propylbenzene	31	8.94
1,3,5-Trimethylbenzene	25	7.15
1,2,4-Trimethylbenzene	38	1.07
Decane	56	16.1
1,4-Dichlorobenzene	13	3.58
1,3-Dichlorobenzene	25	7.15
1,2-Dichlorobenzene	19	5.36

reported in similar thermal desorption applications to analyse trace VOCs [11]. The best limits were obtained for aromatic and aliphatic hydrocarbons and the worst for chlorinated hydrocarbons, depending on detector response. The same compound shows different limits of detection in coal and fly ash/slag due to the different split ratios employed in the thermal desorption method. In the ATD-400 system a split point may be installed at the inlet to the cold trap. This inlet split can be used to enable independent control of tube and trap flow and to restrict the percentage of sample in the tube from reaching the cold trap. In our study this inlet split was closed. A second split installed at the outlet the cold trap allows desorption flows of the cold trap to be compatible with capillary flow rate and to restrict the percentage of sample in the cold trap from reaching the chromatographic column. In this study split ratio in coal samples was fixed at 1:10. Lower ratios allow greater amounts of sample to reach the column, but that involves an increase in the interferences and can lead to detector saturation for main compounds. Fly ash and slag samples are cleaner, thus allowing to work with lower ratios and to increase sensitivity.

### Method precision

The precision of the proposed method was tested by performing six consecutive analyses of six samples of coal, fly ash and slag, employing samples type C. Table II shows the distribution of results obtained. The values of relative standard deviation (% RSD) may be considered good enough due to the fact that precision of the entire processes: extraction and analysis.

**Table II.** Precision of the proposed method (%RSD) tested with sample type C.

	Coal	Fly ash	Slag
1,2-Dichloroethane	–	10.1	–
Benzene	4.1	4.7	3.9
Heptane	–	–	–
Bromodichloromethane	–	–	–
Toluene	6.8	3.0	4.2
1,1,2-Trichloroethane	–	–	–
Dibromochloromethane	–	–	–
Octane	2.1	4.3	–
Tetrachloroethene	5.9	6.3	6.5
Ethylbenzene	5.9	5.7	5.6
m+p-Xylene	4.3	5.7	5.6
Styrene	6.9	6.7	6.8
o-Xylene	4.4	4.1	4.3
1,1,2,2-Tetrachloroethane	–	–	–
Isopropylbenzene	7.6	12.0	–
n-Propylbenzene	15.4	9.0	9.2
1,3,5-Trimethylbenzene	6.3	6.7	6.9
1,2,4-Trimethylbenzene	4.1	4.8	5.3
Decane	4.8	5.1	5.2
1,4-Dichlorobenzene	–	–	6.4
1,3-Dichlorobenzene	–	–	–
1,2-Dichlorobenzene	–	–	–

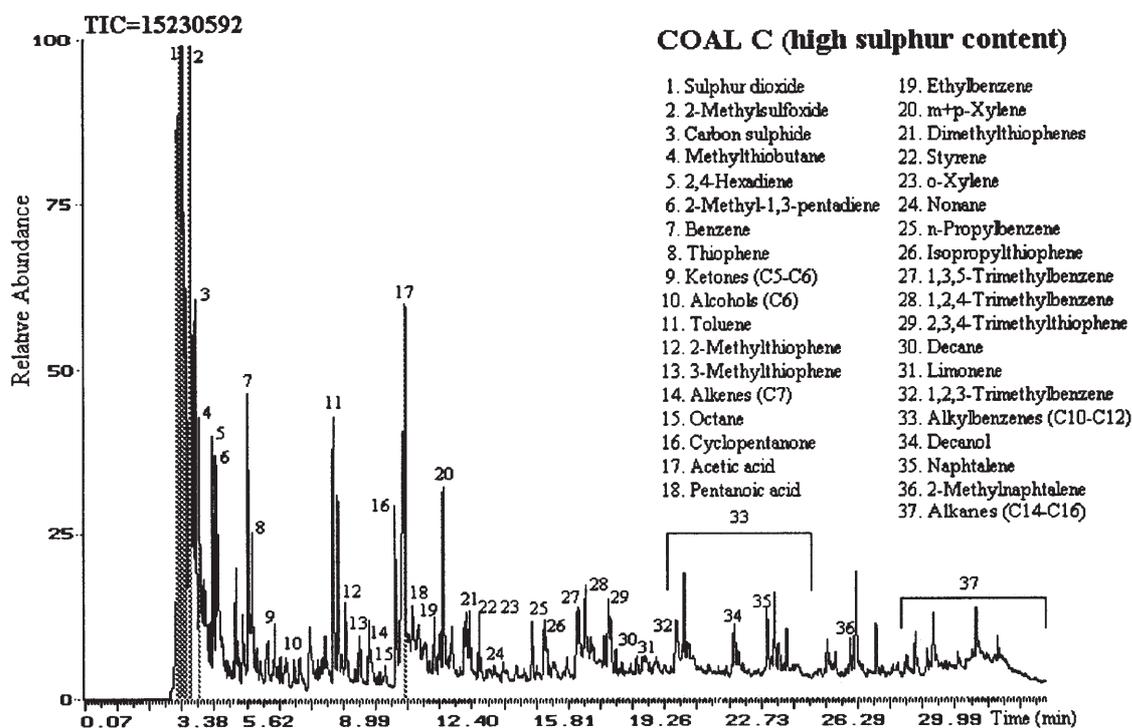
### Qualitative analysis

Several families of compounds were identified in coals: sulphur dioxide, aromatic and aliphatic hydrocarbons, aldehydes, ketones and acids. These results are in accord with those obtained by other authors using other analytical techniques: thermal analysis, solvent extraction, supercritical fluid extraction, spectroscopic techniques [6-9]. Sulphur compounds were more abundant in coals with high sulphur content like C or D. Figure 1 presents a typical chromatogram of a coal with high sulphur content using direct thermal desorption. Other coals with lower sulphur content (A, B, E) present a few peaks corresponding to sulphur compounds as figure 2 shows.

An acetic acid peak was detected in all coal samples. Its origin may be from oxidation processes of the organic matter in the coal. Li *et al.*, 1997 [12] identify acetic acid and other carboxylic acids as trapped compounds in coal by solvent extraction coupled with gas chromatography and mass spectrometry. Chromatograms of figures 1 and 2 also show compounds of natural origin like limonene or camphene.

### Quantitative analysis

Although the compound profiles found in coal samples were very different (see Fig. 1 and 2), main quantified VOCs in

**Figure 1.** Typical chromatogram of gas desorbed from a coal sample type C with high sulphur content.

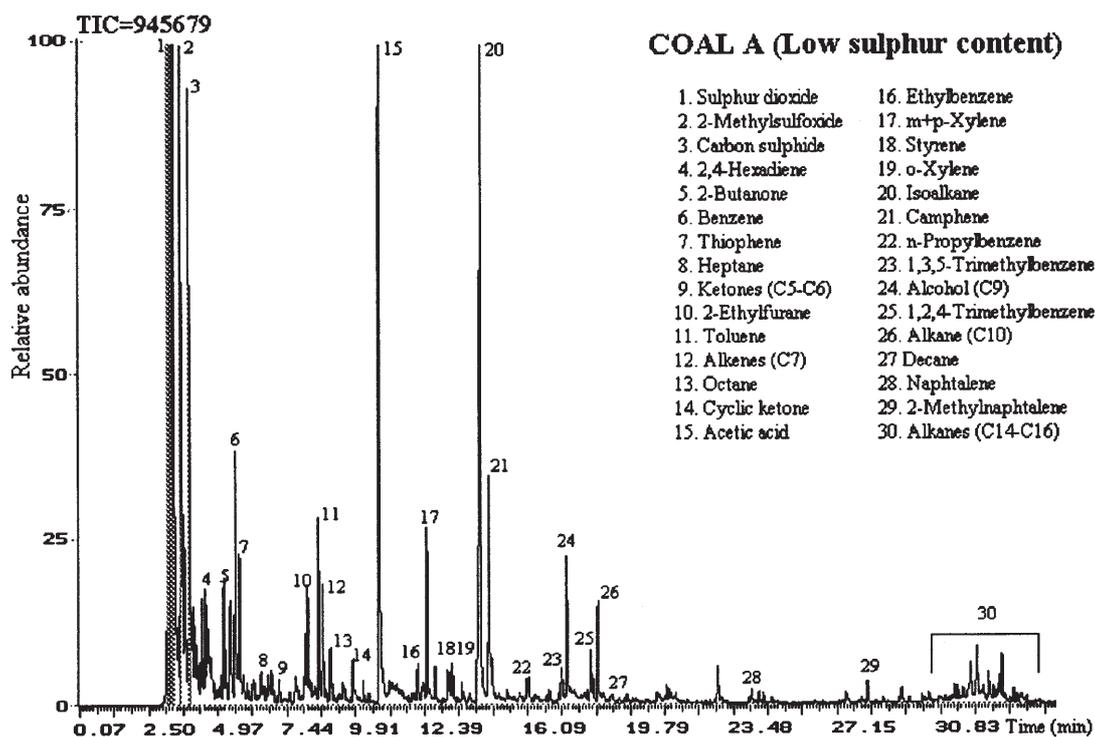


Figure 2. Typical chromatogram of gas desorbed from a coal sample type A with low sulphur content.

these samples were similar for all types of coal as table III shows. Benzene and toluene are the most plentiful compounds with concentrations ranging between 8-25  $\mu\text{g/g}$  (benzene) and 12-40  $\mu\text{g/g}$  (toluene). Xylenes, ethylbenzene and trimethylbenzenes are also detected, although their levels do not usually reach 10  $\mu\text{g/g}$ .

Decane is the most abundant aliphatic in coal samples, although octane is an abundant compound in coal A analysis. Chlorinated hydrocarbons may be missing or be below the detection limit.

Similar levels of volatile hydrocarbons were found in different types of coal. However, D coal usually presents the lowest levels because it is a mixture of coal/limestone (60:40) to feed a fluidised bed power station.

Important variations in VOC levels were observed in samples from the same type of coal which were taken in several sampling campaigns during a one year period. This variation can reach 60 % for several compounds. However, no significant changes were observed during the sampling campaign in macroscopic parameters of coal (%C, %S, etc.). These variations may be due to differences in coal supplying or storage conditions.

Analysis of fly ash and slag samples show that their VOC levels are approximately 10 times lower than those in coal

samples (Tab. IV-V). This is due to the fact that the most important volatile organic fraction is transformed during the combustion process. Benzene and toluene are the most abundant compounds with concentration values ranging between 1 and 3.5  $\mu\text{g/g}$ . Slag and fly ash analysis also presents important differences between samples. This different behaviour can be attributed to differences in coal feed and variations in combustion processes. Other important compounds in fly ash and slag samples were alkylbenzene hydrocarbons, although their concentrations do not usually reach 0.5  $\mu\text{g/g}$ . Heptane is the most abundant aliphatic hydrocarbon, specially in ash and slag produced by coal B, although this compound presents an irregular behaviour, having limit of detection values below 3  $\mu\text{g/g}$ .

One of the most important differences between fly ash/slag and coal samples is the halogenated hydrocarbon pattern. These compounds (1,2-dichloroethane, tetrachloroethene and chlorobenzene) are below the detection limits in coal samples but they are detected in slag and specially in fly ash samples, although their concentration does not exceed 1  $\mu\text{g/g}$ . Chlorinated hydrocarbon levels are more important in fly ash A, C, E. Moreover, in these samples trichloroethene, dichloromethane, 1,1-dichloroethylene or bromodichloromethane were identified by mass spectrometry.

**Table III.** VOCs concentration ( $\mu\text{g/g}$ ) in coal samples (mean  $\pm$  SD).

	<i>Coal type A</i> (n = 3)	<i>Coal type B</i> (n = 4)	<i>Coal type C</i> (n = 6)	<i>Coal type D</i> (n = 4)	<i>Coal type E</i> (n = 5)
1,2-Dichloroethane	ND	ND	ND	ND	ND
Benzene	7.25 $\pm$ 2.00	14.83 $\pm$ 3.99	13.17 $\pm$ 15.64	7.56 $\pm$ 3.57	26.9 $\pm$ 11.04
Heptane	4.23 $\pm$ 5.05	3.02 $\pm$ 6.05	ND	0.27 $\pm$ 3.30	5.30 $\pm$ 3.53
Bromodichloromethane	ND	ND	ND	ND	ND
Toluene	12.31 $\pm$ 3.76	18.86 $\pm$ 1.33	40.11 $\pm$ 16.20	12.13 $\pm$ 3.27	26.82 $\pm$ 10.68
1,1,2-Trichloroethane	ND	ND	ND	ND	ND
Dibromochloromethane	ND	ND	ND	ND	ND
Octane	12.21 $\pm$ 9.17	0.70 $\pm$ 0.81	15.66 $\pm$ 10.28	0.53 $\pm$ 1.22	12.91 $\pm$ 17.74
Tetrachloroethene	ND	ND	ND	ND	ND
Ethylbenzene	1.86 $\pm$ 0.44	1.21 $\pm$ 0.29	3.47 $\pm$ 2.06	1.91 $\pm$ 1.24	3.85 $\pm$ 1.53
m+p-Xylene	4.67 $\pm$ 1.65	5.21 $\pm$ 0.90	19.25 $\pm$ 6.17	4.57 $\pm$ 1.31	11.61 $\pm$ 5.28
Styrene	7.01 $\pm$ 7.34	1.19 $\pm$ 0.15	16.24 $\pm$ 9.99	2.40 $\pm$ 0.73	5.36 $\pm$ 3.25
o-Xylene	3.65 $\pm$ 1.85	1.34 $\pm$ 0.40	2.23 $\pm$ 0.51	1.29 $\pm$ 0.59	4.59 $\pm$ 2.20
1,1,2,2-Tetrachloroethane	ND	ND	ND	ND	ND
Isopropylbenzene	ND	ND	ND	ND	ND
n-Propylbenzene	0.79 $\pm$ 0.31	0.33 $\pm$ 0.09	1.84 $\pm$ 0.45	0.83 $\pm$ 0.64	1.24 $\pm$ 0.64
1,3,5-Trimethylbenzene	1.81 $\pm$ 1.12	3.43 $\pm$ 0.71	1.54 $\pm$ 0.89	0.30 $\pm$ 0.71	1.03 $\pm$ 0.49
1,2,4-Trimethylbenzene	4.06 $\pm$ 1.25	1.61 $\pm$ 0.51	8.13 $\pm$ 5.67	1.45 $\pm$ 0.66	5.62 $\pm$ 2.55
Decane	9.56 $\pm$ 5.84	2.90 $\pm$ 3.18	7.99 $\pm$ 5.78	2.06 $\pm$ 0.79	4.92 $\pm$ 2.55
1,4-Dichlorobenzene	ND	ND	ND	ND	ND
1,3-Dichlorobenzene	ND	ND	ND	ND	ND
1,2-Dichlorobenzene	ND	ND	ND	ND	ND

ND: not detected.

*n* = number of samples.

Values without standard deviation indicate that these compounds appear in only one sample.

**Table IV.** VOCs concentration ( $\mu\text{g/g}$ ) in fly ash samples (mean  $\pm$  SD).

	<i>Coal type A</i> (n = 3)	<i>Coal type B</i> (n = 4)	<i>Coal type C</i> (n = 6)	<i>Coal type D</i> (n = 2)	<i>Coal type E</i> (n = 6)
1,2-Dichloroethane	0.06 $\pm$ 0.04	0.05 $\pm$ 0.03	0.08 $\pm$ 0.05	ND	0.08 $\pm$ 0.05
Benzene	2.45 $\pm$ 2.34	2.12 $\pm$ 0.72	3.36 $\pm$ 1.31	0.15 $\pm$ 0.02	3.27 $\pm$ 1.78
Heptane	ND	0.77 $\pm$ 0.31	1.40 $\pm$ 0.50	ND	1.48 $\pm$ 0.90
Bromodichloromethane	ND	ND	ND	ND	ND
Toluene	2.94 $\pm$ 2.15	0.95 $\pm$ 0.47	1.61 $\pm$ 0.63	0.16 $\pm$ 0.01	2.66 $\pm$ 1.79
1,1,2-Trichloroethane	ND	ND	ND	ND	0.24
Dibromochloromethane	ND	ND	ND	ND	ND
Octane	ND	0.16 $\pm$ 0.08	0.36 $\pm$ 0.30	ND	ND
Tetrachloroethene	ND	0.10 $\pm$ 0.03	0.12 $\pm$ 0.06	ND	0.24 $\pm$ 0.27
Ethylbenzene	0.18 $\pm$ 0.11	0.11 $\pm$ 0.03	0.11 $\pm$ 0.04	0.03 $\pm$ 0.01	0.42 $\pm$ 0.45
m+p-Xylene	0.42 $\pm$ 0.18	0.20 $\pm$ 0.026	0.28 $\pm$ 0.12	0.06 $\pm$ 0.01	0.94 $\pm$ 0.74
Styrene	0.21 $\pm$ 0.04	0.11 $\pm$ 0.03	0.17 $\pm$ 0.07	0.07 $\pm$ 0.02	0.23 $\pm$ 0.19
o-Xylene	0.29 $\pm$ 0.15	0.10 $\pm$ 0.03	0.13 $\pm$ 0.07	0.03 $\pm$ 0.01	0.15 $\pm$ 0.08
1,1,2,2-Tetrachloroethane	ND	ND	ND	ND	ND
Isopropylbenzene	0.02 $\pm$ 0.007	ND	ND	ND	ND
n-Propylbenzene	0.06 $\pm$ 0.02	0.05 $\pm$ 0.01	0.04 $\pm$ 0.02	0.01	0.07 $\pm$ 0.04
1,3,5-Trimethylbenzene	0.10 $\pm$ 0.03	0.05 $\pm$ 0.04	0.04 $\pm$ 0.02	0.02	0.05 $\pm$ 0.03
1,2,4-Trimethylbenzene	0.47 $\pm$ 0.28	0.20 $\pm$ 0.09	0.17 $\pm$ 0.07	0.11 $\pm$ 0.01	0.42 $\pm$ 0.45
Decane	ND	0.33 $\pm$ 0.18	0.38 $\pm$ 0.39	0.06 $\pm$ 0.02	0.37 $\pm$ 0.40
1,4-Dichlorobenzene	ND	ND	0.02 $\pm$ 0.01	ND	0.02 $\pm$ 0.01
1,3-Dichlorobenzene	ND	ND	ND	ND	ND
1,2-Dichlorobenzene	ND	ND	ND	ND	ND

ND: not detected.

*n* = number of samples.

Values without standard deviation indicate that these compounds appear in only one sample.

There are two possible reasons to explain the presence of chlorinated compounds in fly ash and slag but not in coal samples:

a) The lower limits of detection obtained for slag and fly ash samples as table I shows. The best limits of detection found in these samples can explain the lower split ratio employed in their method. Inferior split ratios to avoid interference substances and detector saturation cannot be used in coal samples in the majority of VOCs as mentioned above.

b) Garcia *et al.* [1] propose a mechanism to explain the formation of chlorine compounds. The coal contains trace amounts of chlorine (a few mg kg<sup>-1</sup> or g kg<sup>-1</sup>, depending on the origin) mainly as NaCl, KCl, MgCl<sub>2</sub>, CaCl<sub>2</sub> and associated to organic matter. The chlorine is released during combustion in the form of gaseous hydrogen chloride. HCl can react with organic matter (*i.e.* ethylene) to form chloroethene, trichloroethene, tetrachloroethene, etc. In the same way, chlorobenzenes are formed from benzene. These compounds formed during the combustion processes can be emitted in the gaseous effluent by the stack or trapped in fly ash or slag.

The proposed method removes some of the limitations inherent to these extraction procedures (the formation of artifacts, the need to pre-concentrate samples prior to analysis, and the possibility of sample contamination by solvents). These disadvantages have been confirmed for VOC analysis

in solid samples like vegetal or soils [7,13]. Other studies on organic pollutants show poor recoveries to more volatile fraction due to the different steps of the analytical procedure: extraction, clean up and concentration [14].

## Conclusions

The proposed method for quantifying volatile organic compounds trapped in coal, fly ash and slag samples by direct thermal desorption/gas chromatography/mass spectrometry is both precise and sensitive and has the advantages over classical extraction with organic solvents that it requires only a relative short analysis time and practically no sample handling.

This method is suitable, together with gaseous emissions analysis, for studying the volatile organic compounds distribution during coal combustion in power generation.

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**Table V.** VOCs concentration (µg/g) in slag samples (mean ± SD).

	Coal type A (n = 1)	Coal type B (n = 4)	Coal type C (n = 4)	Coal type D (n = 2)	Coal type E (n = 6)
1,2-Dichloroethane	ND	ND	ND	ND	ND
Benzene	0.63	3.19±2.01	3.02±1.92	0.09±0.05	3.02±2.84
Heptane	2.03	2.96±1.47	1.97±0.61	ND	2.17±1.27
Bromodichloromethane	ND	ND	ND	ND	ND
Toluene	1.58	3.31±2.01	2.93±2.31	0.04±0.02	2.70±1.97
1,1,2-Trichloroethane	ND	ND	ND	ND	ND
Dibromochloromethane	ND	ND	ND	ND	ND
Octane	ND	ND	ND	ND	0.03
Tetrachloroethene	ND	0.11±0.12	0.18±0.11	ND	0.15±0.13
Ethylbenzene	0.15	0.13±0.08	0.18±0.21	0.01±0.01	0.17±0.19
m+p-Xylene	0.41	0.32±0.13	0.49±0.45	0.02±0.01	0.45±0.39
Styrene	ND	0.15±0.14	0.19±0.08	0.03±0.02	0.17±0.08
o-Xylene	0.26	0.17±0.07	0.25±0.21	ND	0.24±0.19
1,1,1,2-Tetrachloroethane	ND	ND	ND	ND	ND
Isopropylbenzene	ND	ND	ND	ND	0.02
n-Propylbenzene	0.05	0.05±0.017	0.04±0.03	0.01	0.03±0.02
1,3,5-Trimethylbenzene	ND	0.08±0.034	0.04±0.14	0.03±0.03	0.04±0.02
1,2,4-Trimethylbenzene	0.4	0.22±0.12	0.23±0.32	0.03±0.03	0.22±0.17
Decane	ND	0.48±0.27	0.57±0.03	0.02±0.02	0.38±0.16
1,4-Dichlorobenzene	ND	ND	0.04	ND	0.04±0.03
1,3-Dichlorobenzene	ND	ND	ND	ND	ND
1,2-Dichlorobenzene	ND	ND	ND	ND	ND

ND: not detected.

n = number of samples.

Values without standard deviation indicate that these compounds appear in only one sample.

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