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Analysis of Airborne Volatile Organic Compounds of a Steel Industry by Solid Phase Microextraction and Gas Chromatography/Mass Spectrometry

F. V. Parreira,[1,2] C. R. de Carvalho,[1,2] Z. de Lourdes Cardeal[1]

[1] Chemistry Department, ICEx, Federal University of Minas Gerais, C.P. 702, 31270-901 Belo Horizonte, MG, Brazil
[2] Fundação Centro Technológico de Minas Gerais, Setor de Medições Ambientais Belo Horizonte, MG, Brazil

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The demand for sampling and analysis of airborne organic pollutants is increasing due to a number of new regulations and also to updating of the regulations in effect through the inclusion of new organic compounds. One of the classes of controlled pollutants is volatile organic compounds (VOCs), owing mainly to the toxic effects they have on man and the environment. Exposure to airborne VOCs can cause headaches; irritations of the eyes, nose, throat mucosae and skin (ALA et al. 1994). The principal source of VOCs in the steel industry is coke. Therefore, coke making and steel making blast furnace gaseous effluents contain phenols, benzenes, toluene, xylene and polynuclear aromatic compounds.

Conventional sampling of airborne VOCs normally uses a solid sorbent and whole air sampling methods (Camel and Caude 1995). Analytes were extracted and concentrated by passing air through a solid sorbent, such as activated/graphitized carbon or porous polymers, followed by thermal or solvent desorption of the analytes. This extraction technique usually requires delicate instruments, is expensive, uses toxic solvents and is time consuming (Camel and Caude 1995; Koziel 1999). When it uses whole air sampling, it involves collecting air matrix into plastic bags or deactivated containers followed by direct injection. Direct syringe injection into chromatographer gives low sensibility. If trace components have to be detected, the air contained within bags needs to be concentrated into a cryogenic trap (Camel and Caude 1995).

An alternative to the concentration of VOCs in whole air collection methods is to use solid phase microextraction technique (SPME), which is less expensive, reutilizable, portable, of easy operation and automation, with minimum loss and contamination of the sample during the transport and storage and a great diversity of sorption phases (Pawliszyn 1997).

The feasibility of the SPME technique for gaseous matrices has been shown previously (Chai 1995; Chai 1998; Koziel 1999; Huali et al. 2002). SPME combines passive mode sampling in and pre-concentration of analytes in a single step, and allows the direct transfer of analytes into a gas chromatograph.

Correspondence to: Z. de Lourdes Cardeal

This paper presents an application of the SPME technique to evaluate the contamination of air by VOCs in the steel industry environment using GC coupled to mass spectrometry (MS).

MATERIALS AND METHODS

The place chosen for sampling was a Brazilian steel industry. Four air samples were collected in 1L Tedlar® gas sample bags (SKC Inc., Eight-Four, PA) by means of a Teflon diaphragm pump.

For the SPME method, a manual holder with PDMS/DVB 65-µm-fiber assemblies purchased from Supelco (Bellefonte, PA) was used for whole air sample concentration/injection. The fiber was exposed to air samples for 60 minutes at 24°C ± 1. After exposure it was retreated into the needle and kept cold. Next, it was inserted into the GC injector for thermal desorption and analysis. A blank of the SPME fiber was carried out before each air sample analysis to check memory effect and also to condition the SPME fiber to the next sample. Direct injection of a sample of 100.0 µL of whole air also was done for comparison by using a Hamilton gas tight syringe (Reno, NE).

For the analysis of the solid waste, 1.00 g of waste was transferred to the calibrated 22.0-mL headspace vial. A PDMS/DVB 65-µm fiber was exposed to the solid waste sample for 60 minutes at 30°C for the absorption of the analytes before GC/MS analysis. The temperature of 30°C was chosen for extraction experiments with SPME, because the amount of compound absorbed by the fiber is inversely proportional to the temperature (Pawliszyn 1997).

GC/MS analysis in scan mode was carried out with an HP 5890 gas chromatographer coupled with an HP 5971A quadrupole mass spectrometer (Hewlett Packard Company, Avondale, PA). The injections were made manually in the splitless mode at 250°C with closed purge for five minutes. The separations of VOCs were made using a 25 m x 0.20 mm x 0.33 µm HP Ultra 2 column (cross-linked 5% phenylmethylsilicone) The oven program began at 35°C, was raised to 280°C at a rate of 10°C/min and held at this temperature for 5 min. The GC/MS interface temperature was 290°C. The sample compounds were identified with the help of an 138 K Wiley electronic library.

The microextraction procedure was carried out by inserting the SPME syringe into the sample bag through a septum, and exposing the fiber for 60 minutes at 24°C for absorption. Next, the compounds were desorbed for 5 minutes at 250°C into the chromatographer injector.

RESULTS AND DISCUSSION

No compounds were detected through the direct injection of 100.0 µl of the air sample into GC-MS, probably due to the low concentration of the compounds in the sample and the low sensibility of the GC/MS system when it operates in the scan mode. However, the analysis of the air samples by SPME-GC-MS identified many VOCs. The compounds were classified as phenol, amide aliphatic, hydrocarbon, and aromatic groups. The most abundant compounds are shown in Table 1.

The VOCs identified, naphthalene and N,N-dimethyl acetamide are among the 188 pollutants controlled by the United States Clean Air program (Keith 1996) and, also, by several institutes of occupational health and industrial hygiene in the world. Figure 1 shows the chromatogram of air sample number 1.

Table 1. VOCs identified by SPME – GC/MS in air samples of a steel industry.

Air sample identification	Identified VOCs
1	1,2-benzenedicarboxylic acid; bis(2-methylpropyl) ester; (1-butylheptyl)-benzene; (1-butyloctyl)-benzene; N,N-diethyl-formamide; N,N-dimethyl-acetamide; 2-nitro-phenol; pentadecane; (1-penthylheptyl)-benzene; (1-propyloctyl)-benzene; tetradecane.
2	(1-butylheptyl)-benzene; (1-butylhexyl)-benzene; (1-butyloctyl)-benzene; decamethyl-ciclopenta-siloxane; N,N-dimethyl–acetamide; (1-ethyloctyl)-benzene; (1-etylnonyl)-benzene; (1-methylnonyl)- benzene; 2-nitro-phenol; pentadecane; (1-pentylheptyl)-benzene; (1-pentylhexyl)-benzene; (1-propylnonyl)- benzene; (1-propyloctyl)benzene; (1-propylheptyl)-benzene; tetradecane; tridecane.
3	1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester; decamethyl-cyclopentasiloxane; 2,3-dihydro-5-methyl-1H-indene; N,N-diethyl-formamide; N,N-dimethyl–acetamide; eicosane; heptacosane; 1,3,5-trimethyl-benzene; 1-methyl-naphthalene; naphthalene; 2-nitro-phenol; tetradecane; tricosane.
4	(1-butylheptyl)-benzene; (1-butylnonyl)- benzene; (1-butyloctyl)-benzene; decamethyl-ciclopentasiloxane; N,N-diethyl-formamide; N,N-dimethyl acetamide; (1-ethyldecyl)-benzene; (1-ethylnonyl)-benzene; (1-etyloctyl)-benzene; (1-metylnonyl)- benzene; 2-nitro-phenol; octamethyl-cyclotetrasiloxane; pentadecane; tetradecane; tridecane; (1-pentylheptyl)-benzene; (1-propylheptyl)-benzene; (1-propylnonyl)-benzene; (1-pentyloctyl)-benzene; (1-propyloctyl)-benzene.

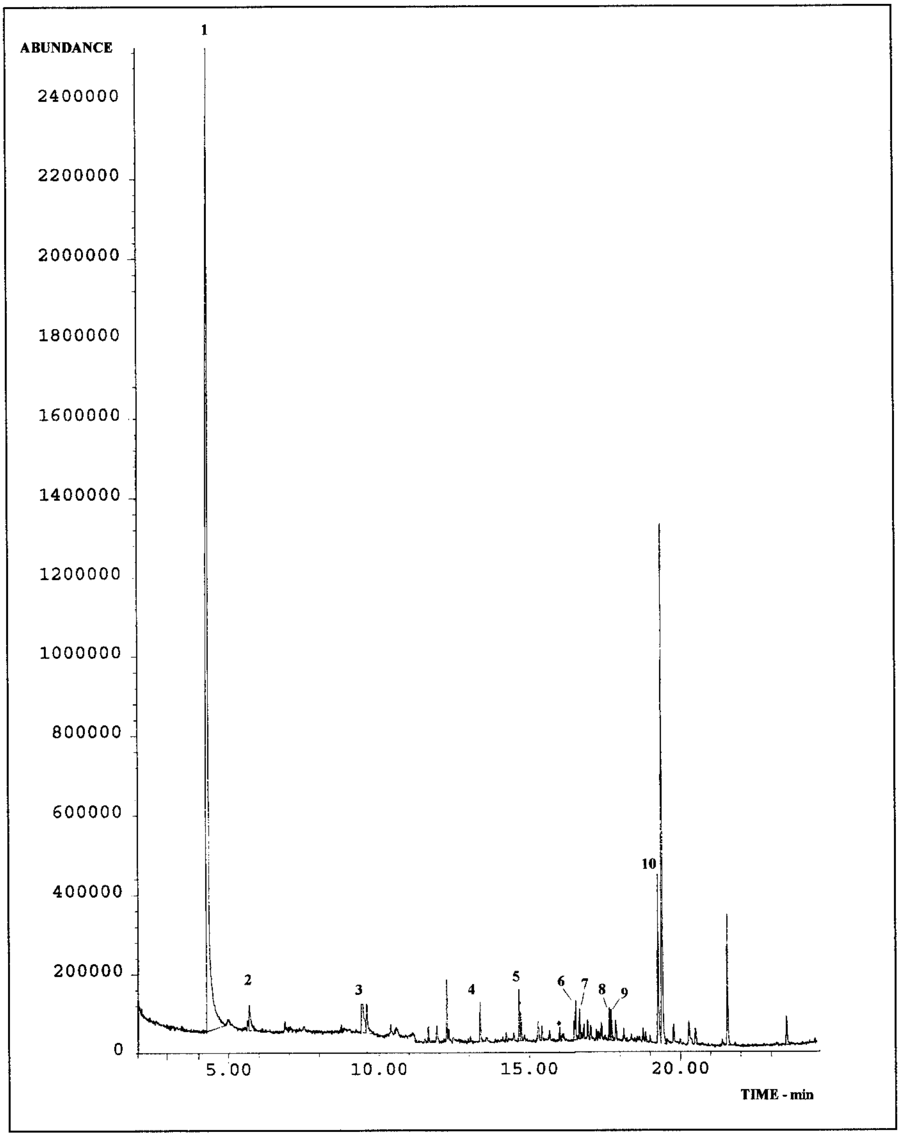

Figure 1 – CG-MS Chromatogram of air sample number 1 after concentration by SPME. Principal compounds identified: 1: N,N-dimethyl acetamide; 2: N,N-diethyl-formamide; 3: 2-nitro-phenol; 4: Tetradecane; 5: Pentadecane; 6: (1-butyl-heptyl)-benzene 7: (1-propyloctyl)benzene; 8: (1-pentylheptyl)-benzene; 9: (1-butyloctyl)-benzene; 10: 1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester.

There was a suspicion that the compounds identified in the atmospheric air and listed in Table 1 would have been released from the solid waste generated in the gaseous effluents treatment station of the steel industry. Therefore, to verify this hypothesis, an analysis of solid waste by GC/MS was conducted. Two solid waste samples from the treatment station were collected in two different places and conditioned inside a glass flask at 3°C. The extraction of VOCs from solid waste is normally carried out by purge and trap or solvent extraction methods. The former requires expensive instruments and is time consuming.

Table 2. VOCs identified by SPME-GC/MS in solid waste samples from the treatment station.

Waste sample identification	Identified VOCs
1	Acetic acid; 4-allyl-1,2-dimethylnaphthalene; azulene; dibenzofuran; 2,3-dihydro-1H-inden-1-one; 4,7-dimethyl-benzofuran; 2,3-dimethyl-phenol; 3,5-dimethyl-phenol; 2,6-dimethoxy-phenol; 2,3-dimethyl-naphthalene; 3,4-dimethoxy-toluene; docosane; eicosane; 2-ethenyl-naphthalene; 4-ethyl-2-methoxy-phenol; 9H-fluorene; hahnfett; heneicosane; heptadecane; hexadecane; hexadecanoic acid methyl ester; 2-methyl-decane; (1-methyldodecil)-benzene; 2-methyl-9H-fluorene; 3-methyl-heptadecane; 3-methyl-hexadecane; 1-methyl-naphtalene; 2-methyl-phenol; 3-methyl-phenol; 9-methyl-9-silafluorene; 2-methoxy-phenol; octadecane; pentadecane; phenanthrene; phenol; 2,6,10,14-tetramethyl-hexadecane; 2,6,10,14-tetramethyl-pentadecane; tricosane; 2,4,6-trimethyl-azulene; 2,4,7-trimethyl-benzofuran; 1,4,6-trimethyl-naphthalene; 2,3,6-trimethyl-naphthalene; 2,4,5-trimethyl-phenol; 2-vinyl-2,3-dihydrobenzofuran.
2	4-allyl-1,2-dimethylnaphthalene; dibenzofuran; 1,1'-biphenyl; 4,7-dimethyl-benzofuran; 2,3-dimethyl-phenol; 2,5-dimethyl-phenol; docosane; eicosane; 4-ethyl-2-methoxy-phenol; 2-ethyl-5-methyl-phenol; 1,4-dimethyl-naphthalene; 1,7-dimethylnaphthalene; 9H-fluorene; hahnfett; heptadecane; hexadecane; 2-methyl-9H-fluorene; 1-methyl-naphthalene; 2-methyl-phenol; 3-methyl-phenol; 2-methoxy-phenol; 9-methyl-9-silafluorene; naphthalene; nonadecane; tridecane; tetradecane; 2,4,7-trimethyl-benzofuran; 2,4,6-trimethyl-phenol; octadecane; pentadecane; phenanthrene; phenol; 2,6,10,14-tetramethyl-hexadecane; 2,6,10,14-tetramethyl-pentadecane; tricosane; 2,4,6-trimethyl-azulene; 2,3,6-trimethyl-naphthalene; 2-vinyl-2,3-dihydrobenzofuran.

The latter uses expensive and toxic solvents, which can result in sample dilution, and thus reduced method sensitivities (Lesage 1993). In this study, the extraction of VOCs present in solid waste samples was accomplished by a SPME method.

The analysis of the solid waste samples by SPME-GC-MS identified many VOCs. The most abundant compounds are given in the Table 2. A comparison of the compounds identified in air and waste solid samples shows that some compounds and a large part of the functional groups are identical, as shown in Table 3 and 4, respectively. Therefore, there is a strong evidence for the contamination of air by the solid waste generated in the treatment station of gaseous effluents.

Table 3. Organic compounds common to air and solid waste samples.

Compound	**Sample number**					
	Air				**Solid waste**	
	1	**2**	**3**	**4**	**1**	**2**
Tetradecane	x	x	x	x		x
Pentadecane	x	x		x		x
Naphthalene			x			x
Tricosane			x		x	x
Eicosane			x		x	x
2,4,6-trimethyl-azulene	x					x

Table 4. Organic functional groups common to air and solid waste samples.

Organic functional group	**Sample number**					
	Air				**Solid waste**	
	1	**2**	**3**	**4**	**1**	**2**
Phenol	x	x	x	x	x	x
Aromatic hydrocarbon	x	x	x	x	x	x
Alifatic hydrocarbon	x	x	x	x	x	x
Carboxylic acid ester	x		x		x	

The results obtained in this work allowed the identification of airborne pollutants in a steel industry, as well as the indication of the most probable source of emission of these compounds. The presence of these VOCs in the air of a steel industry demonstrates the risks of intoxication of the employees themselves as well as of the neighboring populations.

This work showed that it is possible to use the combination of the SPME-GC-MS techniques for the rapid identification of airborne VOCs.

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