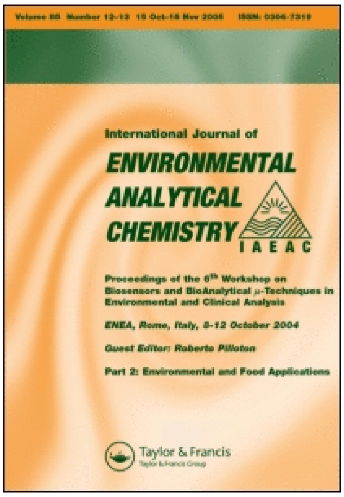

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DETERMINATION OF TOTAL SULPHUR IN LANDFILL GASES USING A QUARTZ CRYSTAL MICROBALANCE

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A method is proposed for the analysis of total sulphur in landfill gases using a quartz crystal microbalance. The performance of the proposed method was tested against the reference method (West-Gaeke method), with standard mixtures, and no significant differences were found between the mean values. The proposed method requires less sophisticated equipment and data treatment than the methods commonly used.

Keywords: Total sulphur; landfill gas; piezoelectric crystal; West and Gaeke method

INTRODUCTION

Sulphur compounds have a notorious odour and may cause adverse effects in air quality and human health. Gas Chromatography-Mass Spectrometry (GC-MS), Gas Chromatography-Flame Photometric Detection (GC-FPD) and Cathodic Square Wave Stripping Voltammetry (CSWSV) [1–5] are some of the methods used for the quantification and speciation of sulphur compounds in the atmosphere. However, all these methods involve sophisticated and expensive equipment, besides cumbersome calculations for obtaining total sulphur content from the speciation data.

This study reports a new method for the quantification of total sulphur in landfill gases, based on an oxidative combustion (total sulphur converted into SO_2), followed by detection of the resulting SO_2 with a quartz piezoelectric crystal microbalance (QCM) [6]. The most important parameters, that control both com-

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bustion and reaction processes, were optimised using a modified simplex method [7,8]. The results are compared with the standard reference method for the determination of sulphur dioxide in the atmosphere (West-Gaeke method)[9].

EXPERIMENTAL

Sampling

Sampling took place in a Portuguese landfill, and a total of 8 samples were collected in October 1998 using Tenax-TA (Chrompack) as adsorbent material. The Tenax (20–35 mesh) was packed in a Teflon tube (60 cm length, 1/16" i.d.). The Tenax bed (10 cm) was hold with two glass wool plugs. Prior to the analysis the Tenax was pre-treated at 350°C overnight. The schematic of the sampling apparatus is shown in Figure 1. The pump used was a Thomas model 107CD18 USA), and the mass flowmeter was from Aalborg instruments (GFM-1700) USA).

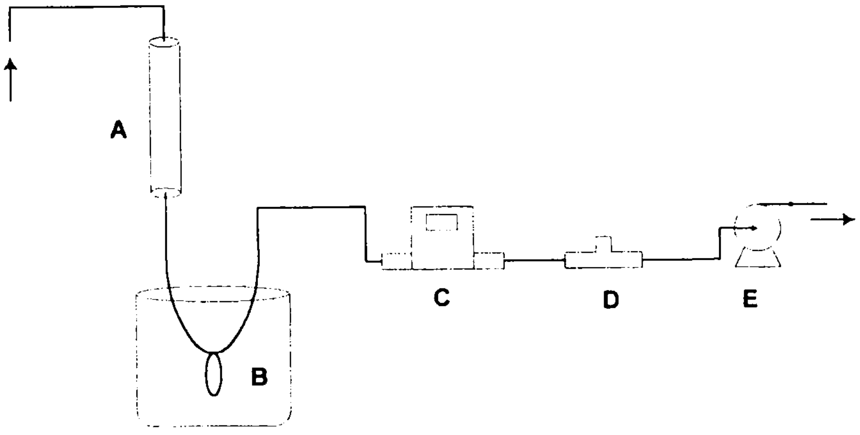

FIGURE 1

Analysis

Figure 2 shows the apparatus used for the analysis of total sulphur following the proposed procedure.

The system used for the oxidation of the sulphur compounds was home made, and consisted of a quartz tube (15 cm × 0.4 cm i.d.) coiled in 19 turns of 0.7 cm of internal diameter. This coil was placed inside a home made tubular oven with

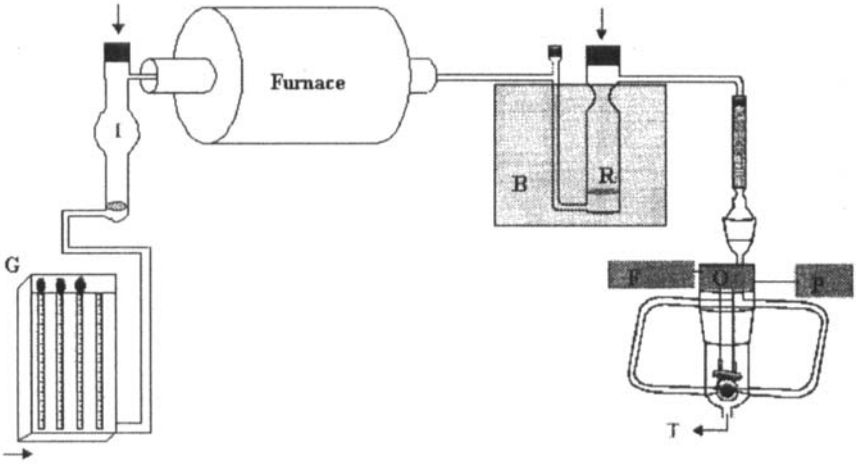

FIGURE 2

a temperature controller Philips Witromat (0–1600°C) (Netherlands). The piezoelectric sensors were quartz crystal AT-cut with gold electrodes (9 MHz) (International Manufacturing Co, Inc, Oklahoma, USA). The frequency meter used was Univolt laboratory 089300 (Japan). The blending of the gases for the standards was accomplished with a gas proportioner frame with there variable area flowmeters (Cole-Parmer, USA).

The standard sulphur compound (1-ethanethiol) was from Sigma-Aldrich and used without further purification.. Mercury nitrate and potassium permanganate were from Panreac (Spain), and nitric acid and magnesium perchlorate were from Riedel-de-Haën (Germany). The gases were nitrogen (N45) and oxygen (045) from Ar Liquido (Portugal).

A volume of 10 cm^3 of a mercury(I) nitrate solution, daily prepared in HNO_3 0.1mol/dm^3, from a stock solution of $HgNO_3.H_2O$ 0.01mol/dm^3 in $HNO_3$0.01mol/dm^3, was introduced into the reaction cell. Due to the disproportionation of mercury, the resulting Hg(0) amalgamates onto the gold electrodes of the piezoelectric sensor, a frequency decrease is observed. As soon as the frequency stabilises, either the sample or the sulphur standards were injected into the injection cell, and carried by the gas mixture (nitrogen and oxygen) through the quartz coil placed inside the furnace.

The sample was desorbed from the Tenax trap by inserting the loop between the gas proportioner and the quartz coil, being flushed with a mixture of nitrogen and oxygen and heated to 100°C. The standards were prepared by injecting different volumes of 1-ethanethiol into the oxidation system. After the oxidative

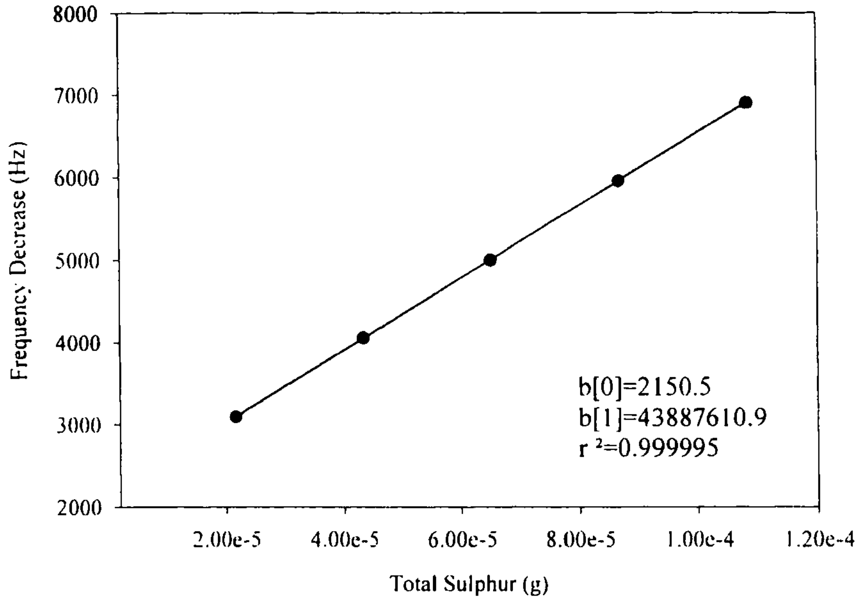

FIGURE 3

combustion, the resulting SO_2 flows into the reaction cell and reacts with the Hg(I) solution. The SO_2 promotes the mercury disproportionation, more Hg(0) is produced and a new frequency decrease is observed, which is proportional to the mass of SO_2 generated, and so to the contents of the sulphur injected. For a matter of safety there are two traps: one with sodium hypochlorite and another with potassium permanganate, for the sulphur compounds and Hg(0), respectively.

The QCM method was previously optimised using a modified simplex method [7,8] and the conditions used were: volume of Hg (I) solution, 0.54 cm^3; bath temperature, 34°C; oxygen flow, 20.2 cm^3/min; total flow, 50.5 cm^3/min; nitric acid volume, 3.64 cm^3; and furnace temperature, 992°C.

The analysis, using the West-Gaeke method, was done according to the literature [9]. The standards being prepared as for the other method.

RESULTS AND DISCUSSION

In order to assess the performance of the proposed method, ten standard mixtures of sulphur compounds were analysed by both the proposed and reference methods and the results are shown in Table I. Statistical analysis of the data have shown the following features: a) analysis of variance have demonstrated a very small analytical error of about 1.6%; b) there is no significant difference ($P=0.064$) between the means obtained with the proposed method and the values from the standard mixtures (Wilcoxon signed rank test); c) there is a significant difference ($P<0.001$) between the means obtained with the proposed and reference methods (paired t-test between means of the two methods).

TABLE I

Standard mixture	*Total Sulphur (μg)*				
	Reference method		*Proposed method*		*Nominal standard mixture value*
	Mean value	*Standard deviation*	*Mean value*	*Standard deviation*	
1	67.0	1.09	69.2	$7^{*}10^{-2}$	69.2
2	49.6	1.13	51.8	$7^{*}10^{-2}$	52.2
3	62.4	1.32	65.1	$6^{*}10^{-2}$	65.1
4	57.4	1.67	59.5	$7^{*}10^{-2}$	60.0
5	57.5	2.01	59.7	$6^{*}10^{-2}$	60.1
6	49.9	1.37	52.3	$7^{*}10^{-2}$	52.3
7	65.5	1.16	67.2	$5^{*}10^{-2}$	67.2
8	65.2	1.20	67.1	$7^{*}10^{-2}$	67.1
9	68.1	1.04	70.1	$5^{*}10^{-2}$	70.9
10	50.9	1.36	53.8	$4^{*}10^{-2}$	53.8

The calibration curve for the proposed method is shown in Figure 3, and it was obtained with the optimised parameters mentioned above [8,9].

The results obtained for total sulphur concentration found in different landfill gas samples, collected in a Portuguese landfill along 1998, were between 2.05 and 2.18 mg/m^3. These concentrations are within the range estimated from data reported by Christensen *et al.* [10]. The analysis of variance of the data do not exclude the possibility that the differences are due to random sampling variability, after allowing for the effects of differences in factor Day ($P<0.090$). The same applies to the differences in the mean values among the different values of the factor Day, since they show no statistical differences ($P=0.126$).

Terpene hydrocarbons, oxygen containing compounds (methanol, ethanol, acetone, acetic ester, hexanal, and acetic acid), aromatic hydrocarbons (benzene and toluene), and chlorinated hydrocarbons (dichloromethane), are known to be present in landfill gases and suspected to interfere in the determination of total sulphur. These compounds were tested by the proposed method at concentrations equal to the maximum found in the literature [10], and it was observed that none of them caused interference.

From all the above results it can be concluded that the proposed method is more accurate than the reference method for the quantification of SO_2. Consequently, the proposed method is particularly suitable for the determination of total sulphur in landfill gases, and when compared with GC-MS, GC-FPD and CSWSV, requires less expensive equipment and less sophisticated data treatment.

Acknowledgements

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