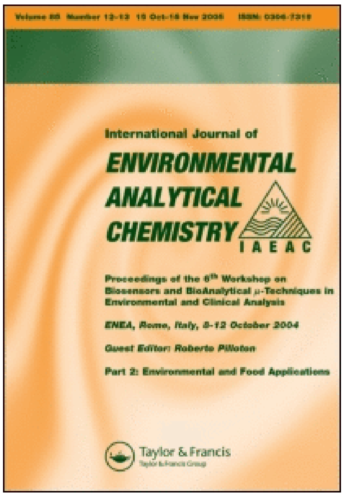

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Application of the Combustion Method in a Closed Flask to the Lead Determination in Atmospheric Aerosols

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The destruction of the filter for metal determination in atmospheric aerosols is an important step in the analysis. Nowadays the decomposition of this kind of sample has not been completely solved, so it is interesting to study new methods for filter sample attack. In the present work the application of the combustion method in a closed flask for mixed cellulose esters filter decomposition for lead determination is proposed. For this purpose optimum operating conditions as stopper flask design, sample size, flask volume, shaking time and volume and concentration of absorbing solution are established, and accuracy and precision of the proposed method using AAS for the measurements is given. The results obtained by the closed flask combustion are compared with those found by wet attack with HNO_3. The method proposed is rapid, has low reagent contamination and no loss of lead by volatilization or by amalgamation occurs. This method shows an accuracy and a precision in good agreement with the standard method.

KEY WORDS: Atmospheric aerosols analysis, lead contamination, filter attack in airborne particulate analysis, closed flask combustion.

INTRODUCTION

The importance of the study of analytical methods for lead determination in atmospheric aerosols is indisputable. Lead is highly toxic even in a very low concentration because of the accumulative behaviour in the human body.[1] Its presence in the environment has an anthropogenic origin. It is used in the manufacture of batteries as well as an additive to internal combustion engine fuels. Taking into account the great toxicity of this element, monitoring of its concentration in airborne particulates is not only desirable but mandatory for industrial areas in developed countries, so a great number of samples must be collected and analysed.

The sampling of airborne particulates is usually carried out by means of mixed cellulose esters filters. Although some authors have proposed other kinds of material for the collection of the sample such as glass fiber filters,[2] porous graphite filters,[3] metal filters[4] and cellulose filters,[5] it seems that mixed cellulose ester filters have advantages on the others for metal determination[6] in such a way that reference methods of the most important Public Health Organisations[7-9] have adopted this material for sample collection in their analytical methods.

Numerous instrumental methods have been applied to the lead determination in air suspended particulates. Most of them have a previous step, that is destruction of the filter in which the sample has been collected. Among the methods used for this purpose, wet attack with HNO_3 or HNO_3—H_2SO_4, dry attack in a furnace at 400–500°C or low ashing temperature utilizing plasma excited oxygen are widely used;[10-12] the first method has the risk of metal contamination from the reagents because of the high concentration of the acids employed, the second has the risk of a possible loss of the more volatile metals and the third is expensive.

In order to study a method for mixed cellulose ester filter attack, the combustion method in a closed flask has been tested. This method was already applied to some metal determination in microsamples of organometallic compounds by Belcher[13] and others[14,15] but no reference has been found for lead determination because of the alloy formed by lead with the platinum sample support.[16] The application of the technique of closed flask combustion to trace metal determination is studied by some authors but in recent years some of them recommended a dynamic technique instead of the so-called static combustion procedure[17] and others propose a partially mechanized method.[18] In the present study and in order to avoid alloy formation with platinum sample support, this material has been substituted by all pyrex glass stopper.

The aim of this work is to evaluate the applicability, precision and accuracy of a rapid method for mixed cellulose ester filter destruction for lead determination in airborne particulates. For this purpose the results obtained by the proposed method are compared with those obtained by wet attack proposed by standard method.[8] In both cases measurements of the lead content in the final solution obtained is carried out by atomic absorption spectrometry. The samples for this study are collected in the urban area of Barcelona (Spain).

EXPERIMENTAL

Apparatus

AAS All measurements were carried out using a Perkin–Elmer atomic absorption spectrophotometer (Model 4000) with double beam and background corrector. Hollow cathode lamp and air-acetylene flame is used.

Combustion flask An all pyrex glass flask and stopper is used. A pear-like form flask of 1000 ml volume is used. The stopper design is described in Figure 1 where dimensions are indicated.

Reagents

Lead stock solution was prepared using ultrahigh purity salt from Merck. Double deionized water, and high purity acids from Merck are used.

Preparation of standards Stock solution of lead ($1.1061\,\mathrm{g\,l^{-1}}$) is prepared from lead acetate, HNO_3 is added to the solution to make pH 1–2. The resulting solution is standardized by complexometry in the usual way: the solution is stored in a polyethylene bottle.

Standard solution $110.61\,\mathrm{mg\,l^{-1}}$ is prepared daily from the stock solution.

Oxygen gas (purity 99.99) is used.

Filter paper

A cellulose acetate ester filter Millipore 0.8 μm pore size, 20 × 25 cm is used. For a tip, filter paper Whatman no. 41 2.0 × 0.3 cm is used.

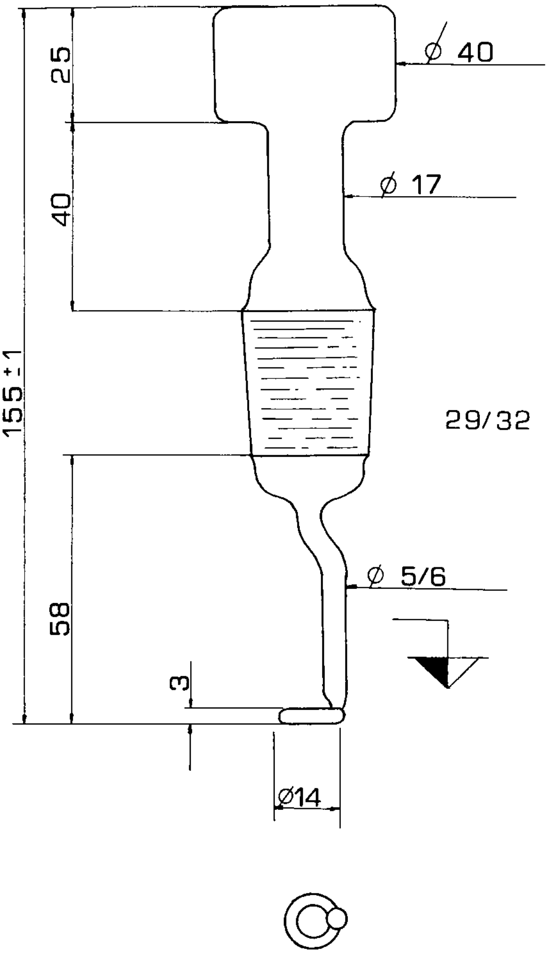

FIGURE 1 All glass stopper design. Dimensions are indicated (mm).

Samples

A high volume air sampler Sierra Misco Inc. model no. 650 with an indicating flow meter is used. Generally the flow-rate used is 1000 m^3/24 hours.

PROCEDURES

For the proposed method

A sample strip of 2.0 × 17.7 cm of mixed cellulose ester membrane filter Millipore, containing 20 mg approximately of particulate atmospheric matter (24 hours collection) is rolled around a little strip (2.0 × 0.3 cm) of Whatman filter paper and placed in the ring of stopper as it is shown in Figure 2. 25.00 ml of absorption solution (HNO_3 1:10) is placed in the flask which is then flushed with a rapid flow of pure gaseous oxygen for a few seconds. By means of the little strip which is used as a tip, the sample is ignited by flame and the flask is stoppered. The combustion is completed in a few seconds and the flask is occasionally shaken for about 20 minutes in order to dissolve in the absorption solution the gases formed in the combustion. The absorbance of the solution obtained is measured by atomic absorption spectrometry at 283.3 nm and using a slit of 0.7 nm, the instrumental conditions are optimized. Six reference solutions are used for calibration, and as a blank, HNO_3 1:10 is used.

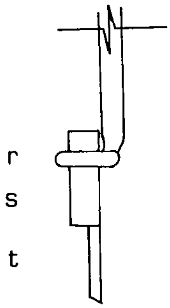

FIGURE 2 Sample strip of 2.0 × 17.7 cm of mixed cellulose ester membrane filter Millipore, placed in the ring of stopper (*r*: ring; *s*: sample strip; *t*: tip).

For wet attack

The procedure described by NIOSH[7] is followed. A sample strip of 2.0 × 17.7 cm is also used. The absorbance of the solution obtained after a suitable dilution is measured according to the procedure described above.

RESULTS AND DISCUSSION

In order to optimize the experimental conditions for the sample combustion in a closed flask several parameters are studied.

Stopper design

As a previous step several kinds of all pyrex stoppers are tested. One stopper with a spiral, another with a hanger and another with a ring. From this test it is concluded that the last form is the strongest and in it the sample roll is easily placed. The diameter of the ring must be optimized for each sample strip size.

Sample size and flask volume

The volume of gases formed in the combustion determines the dimensions of the flask to be used according to the mixed cellulose ester filter sample size. For a strip of 2.0 × 17.7 cm a volume flask of 1000 ml is enough. If a larger filter strip is taken it is necessary to use a bigger flask because of the high pressure developed in the flask.

Another interesting aspect to take into account is the quantity of the airborne particulate collected on the filter. If the content in the sample is smaller than $0.3\,\mathrm{mg\,cm^{-2}}$ the combustion is so fast that it is very difficult to handle, so, at this point it is interesting to know the TSP (total suspended particles) using the same time collection but under different meteorological conditions, and at different height from the ground. As an example, Table I shows the values of TSP collected at the same sampling point in several days after rain (low

TABLE I

TSP (total suspended particulate) ($\mu\mathrm{g\,m^{-3}}$) collected in several days, at the same sampling point, in urban area of Barcelona (1983).

Low contamination						
37.4	28.0	43.3	17.9	55.4	45.2	62.1
28.0	24.3	68.2	33.2	14.2		
High contamination						
124.5	111.6	94.8	76.3	112.5	127.0	103.7
98.0	137.9	157.5	112.8	124.3	169.7	

contamination) and in other days with high contamination, in the urban area of Barcelona.

The test carried out with several sampling times in different meteorological conditons have shown that a 24 hour collection (approx. 0.6 mg cm^{-2} strip content) gives a sample easy to handle with a lead content in the optimum range for AAS measurement; 48 hour collection (approx. 210 mg TSP/filter) gives a final solution not completely clear because of the large concentration of silica which causes problems in AAS measurement, in this case several authors recommended, if necessary, to centrifuge the solution before measurement.[19]

Volume of absorption solution acid and concentration

From the test carried out with several volumes of absorption solution it was concluded that a volume of 25 ml is enough to dissolve all gases formed in the combustion and having previously wetted the walls of the flask in order to decrease the active points of borosilicate glass and consequently to reduce a possible adsorption of lead.

In order to establish the optimum acid concentration in the absorption solution, several HNO_3 concentrations from 2% to 10% are assayed. From the obtained results 10% HNO_3 were established, no higher concentration was used in order to minimize acid contamination.

Shaking time

Once the combustion is completed in about a few seconds, the white gases formed must be dissolved in the solution. To make the absorption easy, the flask must be shaken. After 20 minutes the gases became clear in the flask. The tests carried out at different shaking times showed that 20 minutes are enough for complete absorption.

RSD percent values in analysis of lead in filter strips

From each filter, 10 strips of 2.0 × 17.7 cm are cut. Five of them are analysed by wet attack and the other five by closed flask combustion. Before carrying out AAS measurement of the lead in the final absorption solution, it was tested that the filter has no influence in absorption signal nor in the blank. The relative standard deviations between the five strips analysed using both attack methods and for the 12 filters tested are given in Table II.

TABLE II
Precision of the proposed method and of the acid digestion method.

Filter	Closed flask combustion (% RSD)	Acid digestion (% RSD)
1	6.33	2.58
2	8.20	10.53
3	1.73	6.35
4	7.67	3.15
5	7.57	5.56
6	8.61	9.93
7	12.24	18.85
8	3.48	2.78
9	4.74	3.27
10	7.32	8.98
11	2.92	1.43
12	3.60	3.97
Mean value	6.20	6.45

Accuracy of the method

The accuracy is carried out operating in the same way as described in "precision of the method". The average value of the five strips analysed for each filter, using wet attack and closed flask combustion is given in Table III. The percentage of recovery results for closed flask combustion is referred to the results obtained by wet attack.

CONCLUSIONS

The proposed method, using a closed flask with an all glass stopper has shown it to be a good method for lead determination in atmospheric aerosols collected with mixed cellulose ester filters, as is shown by the accuracy and the precision obtained if compared with

TABLE III

Accuracy by acid digestion and by closed flask combustion. Percent recovery is referred to acid digestion.

Filter	Acid digestion ($\mu g\,m^{-3}$)	Closed flask cumbustion ($\mu g\,m^{-3}$)	Percent recovery
1	1.19	1.05	82.2
2	1.01	1.15	113.9
3	1.49	1.33	89.3
4	1.63	1.40	85.9
5	0.73	0.68	93.2
6	1.07	1.16	108.4
7	0.75	0.98	130.7
8	1.46	1.32	90.4
9	0.70	0.66	94.3
10	0.83	0.81	98.9
11	1.01	0.92	91.1
12	0.97	1.16	119.6

Each result is an average value of five determinations.

acid digestion method, which is recommended as standard for NIOSH[8,9] and APHA.[7]

In addition, this method has advantages as regarding the classical oxygen combustion flask method using platinum support because it eliminates risk of amalgamation. On the other hand, the proposed method has advantages over the other methods (dry ashing, low temperature ashing, acid digestion) used in the destruction of mixed ester cellulose filters, such as rapidity (20 minutes), low cost and low volume of reagents and consequently low metal contamination; and it must be noted that the absorption solution can be directly aspired into the nebulizer chamber without any other manipulation. These advantages make the proposed method very suitable to analyse a great series of samples in monitoring atmosphere quality.

At present more researches are being carried out with other metals.

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