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EDXRF DETERMINATION OF Pb IN AEROSOL SAMPLES FROM MEXICO CITY

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ABSTRACT

The indiscriminate use of automobile transport in high populated cities is one of the major causes of atmospheric pollution. The uncontrolled emissions from automobile engines in the past have made Mexico city one of the most polluted world capitals. Since 1989 the Government started a set of actions as part of the "Program to improve the quality of the air in the Mexico valley". A method for the determination of Pb contents in air particulate matter was developed in the Laboratory of Bacteriology and Physical Chemistry, analyzing high volume aerosol filters by Energy Dispersive X-ray Fluorescence (EDXRF) using a 30 mCi ^{238}Pu excitation source. The performance of the analytical procedure is discussed.

INTRODUCTION

The indiscriminate use of automobile transport in highly populated cities is one of the major causes of atmospheric pollution. Mexico city has been one of the most polluted world capitals during the last decades, and several actions and programs have been carried out to stop and to reduce the atmospheric pollution. The Government started a new set of actions for the period 1995 - 2000 as part of the " Program to improve the quality of the air in the Mexico valley".
In 1989 an agreement was signed between the Universidad Nacional Autónoma de México (UNAM) and the Federal District Government. The main task of the Laboratory consists on the determination of both organic and inorganic pollutants in environmental samples.
The maximum accepted level for the concentration of Pb in particulate matter in air is 1.5 μg Pb/m^3 [**1**]. Several monitoring stations are located in Mexico city following the main direction of the winds [2]. The determination of the amounts of Pb and Mn deposited on glass based aerosol filters was performed at the LBFQ by Atomic Absorption Spectrometry (AAS), since 1989, following the Mexican official norms.
The sampling of airborne particulate matter [3] is mainly performed using large volume collecting devices (1.5 m^3 air/min.) on large area aerosol filters (8"x10"). Thus, the resulting amount of Pb after 24 hours of air sampling (2160 m^3), for the concentration value corresponding to the maximum accepted level, is of approximately 3240 μg. Such amount of Pb can be measured by most of the EDXRF spectrometer arrangements. Besides its simplicity and adequate accuracy and

precision, the determination by EDXRF is advantageous compared to other techniques by the fact that allows to preserve the analyzed sample for control or other further purposes.

MATERIALS AND METHODS

The glass based aerosol filters have an active deposition area of 7" x 9". A major portion of the active area is destined to the analysis of toxic organic compounds and a section of 3" x 7" was routinely analyzed by AAS to establish the concentration levels of Pb and Mn. The followed AAS procedure was not only troublesome, but also implies the total destruction of the sample.

The EDXRF spectrometer consists of a Princeton Gamma Tech. Si(Li) detector (energy resolution 180 eV for Mn-Kα) with a charge sensitive pre-amplifier and the subsequent spectrometric array. Only a 30 mCi ^{238}Pu cylindrical shaped source was available for the excitation of the sample. A holding device (see fig. 2) was designed to allow the excitation of a large area of the filter under 45^{o} of incidence of the excitation radiation, looking to improve the instrumental sensitivity. Figure 1 shows the excitation - measuring geometry. Such arrangement allows to analyze one third of the total active filter area by measuring a 3" x 7" section of the filter folded in three parts.

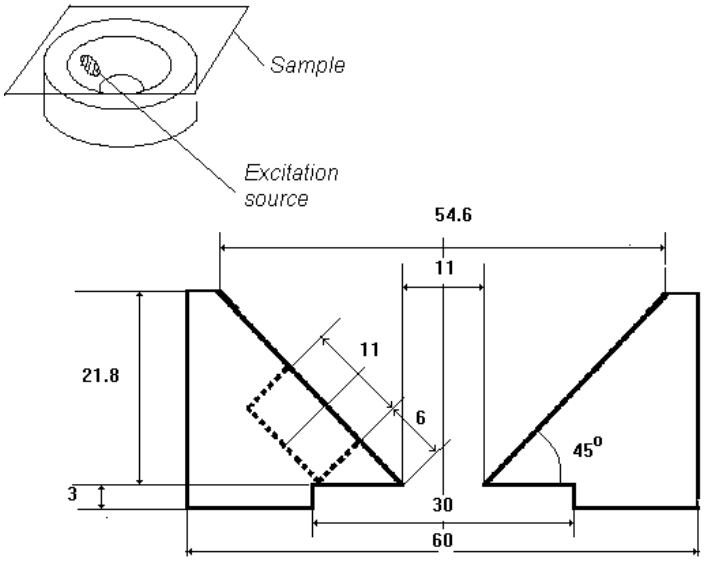


Fig. 2 Geometric arrangement for aerosol filter measurement (all distances are expressed in mm)

The use of ^{238}Pu for excitation is advantageous for the excitation of Pb L-lines, due to the small difference between the average energy of the U-Lα lines (13.6 keV) and the value for the Pb-Lα absorption edge (15.8 keV).

The resulting amount of Pb corresponding to the maximum accepted level in a sample is

$$Pb_{\substack{measured\\sample}}[\mu g] = Accepted\_value\left[\mu g/m^3\right] \times Air\_Sampled\_Volume[m^3] \times \frac{Filter\_Measured\_area}{Total\_Filter\_area} \qquad (1.1)$$

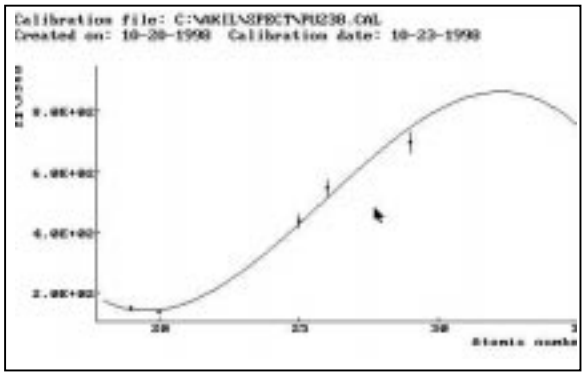
$$Pb_{\substack{measured\\sample}}[\mu g] = \left[1{,}5\,\mu g/m^3\right] \times 2160[m^3] \times \frac{3" x 7"}{9" x 7"} = 1080 \qquad (1.2)$$

The fitting of the measured spectra and quantification was performed using the AXIL-QXAS package [**4**] , which is freely distributed by the International Atomic Energy Agency. A group of compounds of known composition was measured and the calibration of spectrometer sensitivity for K and L lines was performed following the procedure "Elemental sensitivities" included in the algorithm "Simple quantitative analysis". The low aerial density of the analyzed samples (< 0.025 g/cm^2), as well as the "light" composition of the filter matrix allow to consider the "thin sample" approach.

RESULTS AND DISCUSION

Analytic performance.

The results of the calibration of instrumental sensitivities are shown in the figures 3 and 4. The sensitivity values are expressed in counts per second normalized to percent concentration and to the sample mass attenuation coefficient.



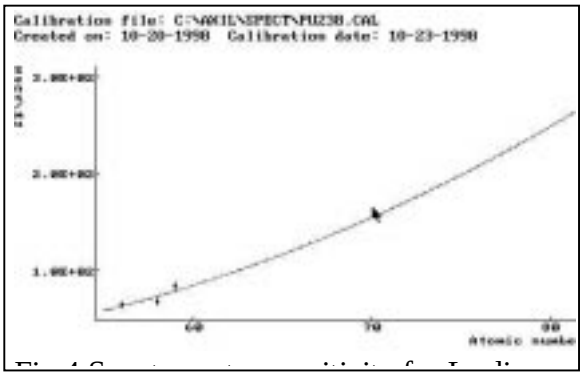


Fig. 4 Spectrometer sensitivity for Lanthanides

The analysis of 3 blanck filter samples showed the presence of several elements and their average concentrations are given in Table 1. None of the elements found in the filter matrix affect the analysis of Pb. The detection limit was evaluated following the IUPAC accepted definition, using 3 times the square root value of background in the region under the Pb-Lα line, for one hour of measurement time. The precision of the determination was evaluated by the comparison of the obtained values with the results of the analysis for a set of samples by AAS. No significant differences were found between the results obtained by both methods (see table 2 and figure 5), with an average bias for the studied concentration range of less than 20 %. The accuracy of the determinations was better than 10 %.

Table 1 Filter impurities

	Average (N=3)	
	µg/g	µg_Tot
K	3376	10129
Ca	5046	15139
Fe	349	1046
Ni	52	155
Cu	129	387
Zn	11853	35560
Br	98	295
Ba	6921	20762
Detection limit		
Pb	27	120

EDXRF	AAS
354	309
148	114
207	159
232	252
124	102
220	261
179	189
105	111
133	132
< 120	< 84
< 120	< 84
< 120	< 84
< 120	< 84
< 120	< 84
< 120	< 84
Average Amount (µg_Tot)	**150,1**
Correlation Coefficient	**0,9513**
Slope of linear regression	**1,001**
Average typical error (%)	**17.3**

Table 2 Comparison of EDXRF and AAS Results

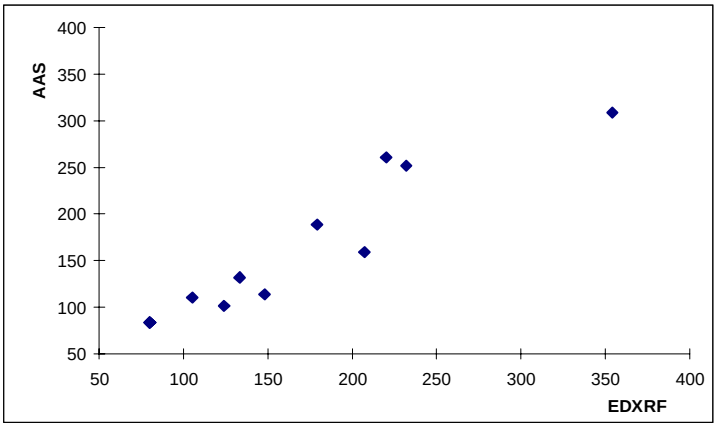


Fig.5 Correlation between results

AKNOWLEDGMENTS

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REFERENCES

[1] PROGRAMA PARA MEJORAR LA CALIDAD DEL AIRE EN EL VALLE DE MEXICO (1995-2000). II. NORMAS DE CALIDAD DE AIRE Y DE SALUD AMBIENTAL.
[2] EVOLUTION OF POLLUTANTS IN MEXICO CITY MEASURED WITH NUCLEAR ANALYTICAL TECHNIQUES. T.MARTINEZ ET AL. 6TH INTERNATIONAL CONFERENCE ON APPLICATIONS OF NUCLEAR TECHNIQUES. CRETE, GREECE. JUNE 20-26, 1999.
[3]NOM-CCAM-002-ECOL/1993.
[4] AXIL-QXAS MANUAL. P.KREGSAMER. IAEA, VIENNA. 1995.