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DEVELOPMENT OF AN ANALYTICAL METHOD FOR THE DETERMINATION OF ELEMENTS IN PARTICULATE MATTER BY MEANS OF ED-XRF

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Abstract: Among the analytical techniques of particular importance for the determination of the content of elements in samples of atmospheric particulates deposited on membranes there is energy dispersive X-ray fluorescence spectrometry (ED-XRF). This method combines the advantages of being rapid, non-destructive, multi-elemental, adequately sensitive and quantitative. The use of polarized radiation allows minimizing the background signal and, consequently, improves the detection limits. The elements determinable through ED-XRF are characterized by atomic number greater than 10. Those on which the interest is focused are: Ag, Al, As, Au, Ba, Bi, Br, Ca, Cd, Cl, Co, Cr, Cu, Fe, Ga, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, Pt, Rb, S, Sb, Se, Si, Sn, Sr, Ti, Tl, V, W, Zn, Zr. In practice, in the current state not all of these elements are determinable with sufficient reliability: for Ag, Ba, Na, P and Sb it was not possible to obtain adequate analysis conditions and the related analytical results cannot be used. Instrumental parameters have been set, and the filter and film support was selected in order to minimize the interferences. The uncertainty of measurement of EDXRF analysis was estimated and also the evaluation of Limit of Detection and accuracy of the method was carried out.

Keywords: ED-XRF, particulate matter, uncertainty, LOD.

1. INTRODUCTION

Among the analytical techniques of particular importance for the determination of the content of elements in samples of atmospheric particulates deposited on membranes there is energy dispersive X-ray fluorescence spectrometry (ED-XRF). This method combines the advantages of being rapid, non-destructive, multi-elemental, adequately sensitive, quantitative analytical technique. The use of polarized radiation allows minimizing the background signal and, consequently, improves the detection limits.

The elements determinable through ED-XRF are characterized by atomic number greater than 10. Those on which the interest is focused are as follows: Ag, Al, As, Au, Ba, Bi, Br, Ca, Cd, Cl, Co, Cr, Cu, Fe, Ga, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, Pt, Rb, S, Sb, Se, Si, Sn, Sr, Ti, Tl, V, W, Zn, Zr. In practice, in the current state not all of these elements are determinable with sufficient reliability: for Ag, Ba, Na, P and Sb it was not possible to obtain adequate analysis conditions and the related analytical results cannot be used. ED-XRF analyzes have been conducted by means of Spectro X-Lab 2000 supplied to the Enel research centre in Brindisi.

2. INSTRUMENTAL STEP

In theory, for each of the elements of interest the optimal working conditions can be identified by appropriately varying the voltage of the X-ray tube, the tube current RX, the secondary target and the time of acquisition of the spectrum. However, in order to have a reasonable analysis time, the elements have been grouped into a set of 4 different operating conditions, chosen according to what is suggested by the manufacturer for the acquisition of optimized lines of fluorescence. The four operating conditions are summarized in the table below.

Table 1: Operating condition

Parameter	1 cond.	2 cond.	3 cond.	4 cond.
Channels	1024	2048	1024	1024
Target	Mo (compton)	Al2O3 (barkla)	Co	HOPG (barkla)
Peak time (µs)	30	30	55	55
Zero Peak Rate (cps)	5000	5000	5000	5000
Energy Range (keV)	25	50	12.5	12.5
Voltage (kV)	40	49.5	30	15
Current (mA)	7.5	6	10	13
Max. Meas.Time	200	400	200	200
First - Last Ch.	670 - 702	0 - 2048	0-1024	0-0
Vacuum	On	On	On	On
Element	Fe-Y /Ba-Bi	Zr-Cs	K-Mn	Na-Cl

3.1 FILTER SELECTION

The amount of atmospheric particulate deposited on filter is generally small, in fact it rarely exceeds one mg, therefore possible contamination of elements already present on the white filters might generate a signal that can overlap the same instrumental signal of the elements present in the particulate.

To minimize the problem, filter types with contamination levels as low as possible have been chosen; after a dedicated study polycarbonate filters *Orthopore* were selected. To keep the problem under control, together with the sampled filters a number of white filters are analyzed to detect any abnormal contamination.

3.2 FILM SUPPORT SELECTION

A support of thin film is always mounted with the sample, in order to keep the filter membrane in place on the sample holder during analysis, to retain liquid, powder or solid residues so as not to pollute the detection system of the spectrometer (the sample is positioned inside the spectrometer face down). Among the many different types of materials available, few of them are endowed with the necessary combination of properties that are useful in this specific application. The suitability of a thin film is a function of the transmission properties of each polymer: this film absorbs part of the fluorescence radiation emitted by the light elements, the thin thickness however minimizes this effect. Another important consideration in the evaluation and selection of a thin film is to detect the levels of impurity.

A polycarbonate film thickness of 5 μM Chemplex (cat. CH-480 Item 1164) has been selected as the most suitable for these determinations. Other types of film (ETNOM) have proved totally unsuitable for this type of applications due to the contamination that characterizes them. Subsequent tests showed that the film TF-240 (polypropylene) show characteristics comparable to or better than the CH-480.

3.3 MINIMIZATION OF NICKEL BACKGROUND SIGNAL

During the development of the method it was noticed that during the acquisition of spectra for filters mounted on 32 mm plastic sample holder very high values of counts for nickel were obtained, in the order of several thousands, even for white filters. This created problems for the determination of this element, raising in a drastic way the limit of detection. The problem is not manifested with the use of the 12 positions sample carousel with the 47 mm aluminum sample holder. Thorough a deeper analysis of the problem conducted with the manufacturer, it was concluded that the signal came from the nickel alloy used in construction of the housing chamber of the samples and the sliding cover, rich in nickel: X-rays incident on the sample pass across the membrane and the sample holder plastic, reached the lid and the fluorescence X of the latter reached the detector. It was therefore necessary to adopt a system which would block such X radiation: "caps" of shielding to be applied to the 32 mm filter holder were constructed, consisting of a structure made of cardboard covered with two layers of aluminum foil. The use of such shielding systems made it possible to lower the background signal of nickel from over 4500 counts to about 700.

4. CALIBRATION

The calibration procedure was carried out for most elements using external standard mono-elemental products from MicroMatter (Vancouver, Canada). Only for the lighter elements (ie by the sodium to sulfur) it has been verified that the slope of the calibration curve is significantly influenced by the "matrix" of the sample itself, and therefore it is preferable to calibrate them directly using the Certified Reference Materials NIST 2783 (for samples collected at receptor sites) and BCR 128 (only for samples collected at emission stack for coal ash power stations).

The standard is mounted on a sample holder in a similar manner as the samples. The process of preparation of the standards cannot be separated from certain sources of error, such as the possibility of introducing the external pollutants following the filter's manipulation. A further source of contamination can result from polycarbonate film or sampling filter used.

4.1 EVALUATION OF THE UNCERTAINTY ASSOCIATED WITH THE CALIBRATION

According to the instructions of the guides LGC/VAM/1998/088 "Protocol for uncertainty evaluation from validation data" and LGC/VAM/2003/032 "Preparation of Calibration Curves - A Guide to Best Practice", the uncertainty associated with calibration was evaluated according to the equation:

$$U_q(\mu g) = \frac{s(I)}{b} \cdot \sqrt{\frac{1}{N} + \frac{1}{n} + \frac{\left(I_0 - \bar{I}\right)^2}{b^2 \cdot ssq}}$$

where:

- $s(I)$ = standard deviation of the residuals,
- b = slope of the calibration curve,
- N = number of replicates for each level,
- n = total number of replicates,
- $I_0 =$ intensity of the i-th,
- $\bar{I} =$ the average of the-th intensity,
- $ssq = \sum_{i=1}^{n}\left(q_i - \bar{q}\right)^2$ = sum of the squares of the differences between the average value of each i-th quantity and amount.

This function represents the confidence interval on the estimated value of quantity.

5. LOD

In order to verify the performance of the method the Detection Limit (MDL-minimum detection limit) was estimated. According to the International Union of Pure and

Applied Chemistry, IUPAC, the detection limit define the concentration or amount of a certain element that gives a signal intensity equal to three times the standard deviation of the background intensity. Mathematically the definition of MDL is then:

$$MDL = 3 \cdot \sigma_{fondo} \cdot \frac{C}{I}$$

where σfondo is the standard deviation of the counts of the background, representing the dispersion of the individual measures with respect to the average background and C/I is a function of the slope of the calibration curve for the element under analysis.

The evaluation of the detection limit for each element was made on five replicates of independent pairs of standard, on zero concentration (white) and on average concentration of the application range (usually 0.5µg) , in which case the MDL is calculated according to the following expression:

$$MDL_{standard} = 3 \cdot \sigma_{fondo(picco\ bianco)} \cdot \frac{C}{I_{standard}}$$

If the background signal, measured in this way, returns not appropriate values , for instance always equal to zero, the standard signal was considered for obtaining the MDL by using the following expression:

$$MDL_{standard} = 3 \cdot \sigma_{fondo(standard)} \cdot \frac{C}{I_{standard}}$$

The results of the application of this analysis should be used as input data for numerical mathematical models. Therefore, it was necessary to define a criterion to give numerical meaning to the concentration where values are not quantifiable (<MDL); it has been defined that the values less than MDL are equal to MDL/2 with an uncertainty equal to MDL/2:

$$C < MDL \rightarrow \quad C = \frac{1}{2} \cdot MDL \pm \frac{1}{2} \cdot MDL$$

As a result, a further definition of detection limit was implemented as the amount of analite by which the measured quantity is 50% of the calibration uncertainty or less.

6. ACCURACY

The accuracy of the method was determined by analyzing a certified reference sample, the NIST SRM 2783: Air Particulate on Filter Media. The values for % recovery of the elements actually detectable are shown in Table below: for the elements with values certified by 0.1 ug up, recoveries are acceptable or good, whereas below this threshold the error is significant .

Table 2: NIST 2783 % Recovery

	nist2783	Certified	Recovery %
Mg	11.58	8.62	134
Al	27.92	23.21	120
Si	67.11	58.6	115
S	1.01	1.05	96
K	4.93	5.28	93
Ca	11.9	13.2	90
Ti	1.58	1.49	106
Fe	28.07	26.5	106
Zn	1.34	1.79	75
Cu	0.29	0.4	73
Mn	0.29	0.32	91
Cr	0.18	0.13	138
Co	0.03	0.01	300
Ni	0.12	0.07	171
V	0	0.05	0

7. REFERENCES

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