

**MULTIELEMENT X-RAY FLUORESCENCE ANALYSIS
OF NATURAL WATERS BY USING A PRECONCENTRATION
TECHNIQUE WITH ION EXCHANGE RESINS**

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Abstract. The analysis of trace element in different kinds of waters is described, using a preconcentration technique on ion exchange loaded filter papers. The filters were analyzed employing an energy dispersive X-ray fluorescence system characterized by radioisotopic excitation sources and gas proportional or semi-conductor detectors. The detection limits of the method were experimentally determined and the elemental levels in typical waters were measured.

1. Introduction

The determination of trace element concentration in waters constitutes an analytical problem of considerable practical importance and of developing interest. In fact it is indispensable for controlling water pollution caused by industrial discharges and has promise for the evaluation of water utilizability for industrial and alimentary purposes.

As an example, Table I gives the maximum admissible concentration of trace elements in drinking water according to the Italian Public Health Law. The application of these laws requires that relatively simple and generally reliable monitoring methodologies be used, which allows both the monitoring staffs and the interested industries to compare the water characteristics with legal requirements.

Usually, for the determination of such small concentrations, analytical techniques

TABLE I
Limiting concentrations (in ppm) of some metals in drinking water
according to the Italian Public Health Law

Element	Concentration (ppm)	Element	Concentration (ppm)
Ag	0.1	Fe	0.3
As	0.05	Hg	0.005
Ba	1.0	Mn	0.05
Cd	0.05	Ni	1.0
Cr III	1.0	Pb	0.05
Cr VI	0.05	Se	0.01
Cu	0.5	Zn	1.0

such as atomic absorption, atomic emission, activation analysis, mass spectrometry, colorimetric methods, electrochemical methods etc. are employed. The X-Ray Fluorescence (XRF) technique has recently achieved considerable importance in the determination of trace elements. The XRF may be induced by protons, by the more common and simple radioisotopic sources emitting low energy X or gamma rays, or by miniaturized X-ray tubes. The XRF technique does not have sufficient sensitivity for directly analyzing liquids, but it does very well for a simple pre-enrichment stadium employing ion-exchange resins or ion exchange resin loaded filter papers. The coupling of ion exchange resins to X-rays energy dispersive fluorescence analysis is very successful as the resins and the filter papers containing resins constitutes an ideal matrix because of the low atomic number of its constituents.

A large body of references is available on the characteristics of the resins and on the employment of ion-exchange resins loaded filter papers coupled to various analytical techniques, while data concerning the coupling of XRF analysis to an enrichment step employing ion exchange resins are still scarce (Holynska *et al.*, 1973; Law and Campbell, 1974; Leyden, 1974; Van Gricken *et al.*, 1976; Smith and Masi, 1976; Wundt *et al.*, 1976).

In this work a systematic study has been carried out on ion-exchange resin loaded papers, using an X-ray energy dispersive equipment. This permits a contemporary quantitative analysis with good precision, simplicity and reproducibility of most of the ions present in solution. Also a systematic study has been conducted on the capturing by the resins of the ions from the solution being filtered and of the optimal pH value.

Finally, all conditions allowing a quantitative determination of the concentration of the ions in different waters have been studied and standardized.

2. Apparatus

Different experimental arrangements have been employed for different kinds of ions. To measure the amount of major ions in water, for example Ca in natural or mineral waters, or ions in industrial effluents, a 'single element' apparatus has been set up. It consists of a gas proportional counter coupled to a sealed-off radioisotopic source, a linear amplification chain, a single channel analyzer and a scaler-timer.

For the analysis of solutions containing a large variety of ions, it is necessary to analyze the filter with a semiconductor detector for X-rays and to employ a multi-channel analyzer. Therefore, we employed for light elements ($Z < 15$, X_K -rays analysis) and for heavy elements ($Z > 75$, X_L -rays analysis) a Si(Li) detector 6 mm diameter \times 3 mm thickness with 180 eV resolution at 5.9 keV and an entrance window of 15 μ m. For the analysis of medium elements ($30 < Z < 60$) a Ge(Li) detector 12 mm diameter \times 3 mm thickness has been used with 400 eV resolution at the 32 keV Ba- X_K peak. For elements having atomic number $Z < 22$, a ^{202}Bi / ^{202}Tl radioisotopic source has been employed. For elements ranging from 20 to about 38 (X_K -rays) and from

TABLE II

Choice of the radioisotopic source and of the detector as a function of the atomic number Z of the element to be analyzed

Z	Radioisotopic source	Detector	
		single element analysis	multielement analysis
16-22 (X_K -rays)	H^{90}/Zr (2 Ci)	Thin window Xe-gas prop. counter	Si(Li)-semiconductor detector
22-35 (X_K -rays)	Pu^{238} (10 mCi)	Xe-gas prop. counter	Si(Li)-semiconductor detector
35-56 (X_K -rays)	Am^{241} (50 mCi)	Xe-gas prop. counter	Ge(Li)-semiconductor detector
45-55 (X_K -escape peaks)	Am^{241} (50 mCi)	Kr-gas prop. counter	
73-92 (X_L -rays)	Pu^{238} (10 mCi)	Xe-gas prop. counter	Si(Li)-semiconductor detector
82-92 (X_L -escape peaks)	Pu^{238} (10 mCi)	Kr-gas prop. counter	

about 75 to 92 (X_L -rays), a 10 mCi Pu^{238} radioisotopic source was employed, and for elements ranging from about 40 to about 60, a 50 mCi Am^{241} source was employed.

A summary of sources and detectors employed in the present work is given in Table II. More details about X-rays detectors and radioisotopic sources can be found in a previous paper (Cesareo *et al.*, 1976).

3. Results and Discussion

In the present study, ion exchange resin loaded filter papers, produced by Whatman Inc. were employed; their characteristics are listed in Table III. Their average atomic number is about $Z = 7$ (deduced by transmission measurements) and their thinness render these filters optimal for XRF analysis as they approximate well samples called 'thin' in literature.

TABLE III
Physical properties of some resin loaded filters

Filter	SA-2	SB-2
Resin type	Amberlite IR-120	Amberlite IRA-120
% Resin in paper	45-50%	45-50%
Resin form	Na^+	Cl^-
Thickness (in mm)	0.35	0.35
Flow rate	fast	fast
Exchange capacity	0.2 meq	0.15 meq
Useful pH range	1-14	0-12

In the case of 'thin samples' one can write that the XRF counts relative to the i -th ions absorbed by the resin filter are given by the expression:

$$N_i = N_0 K \varepsilon(E_2) \omega_i \mu_{\text{P},i} (1 - 1/J_i) C_i m \text{ counts s}^{-1} \quad (1)$$

where N_0 is the number of photons s^{-1} of energy E_1 emitted from the source and directed on the filter, K is the geometric efficiency, $\varepsilon(E_2)$ is the intrinsic efficiency of the detector at energy E_2 corresponding to the X-rays emitted by the element i , ω_i is the fluorescent yield of the i th element and $\mu_{\text{P},i}$ (in g cm^{-2}) is the photoelectric mass absorption coefficient of element i at the energy E_1 , J_i is the absorption coefficient of element i at the energy E_1 edge jump ratio, C_i the concentration of the i th element and m (in g cm^{-2}) is the mass per unit area of the filter.

It can be deduced from Equation (1) that the fluorescent counts N_i are independent of the presence of other elements within large intervals of concentration (Cesareo *et al.*, 1976; Rhodes, 1974), that the fluorescent counts N_i are directly proportional to the mass per unit area of the i th element, and that it is possible to evaluate the concentration of the elements present in the sample to be analyzed by employing only one standard sample of any one of the elements. In fact, from the measurements obtained with such samples, the product $N_0 K$ can be evaluated, and therefore, since ω_i , $\mu_{\text{P},i}$ and J_i are accurately known, it is possible to deduce the concentration of any other of the elements present in the filter, as long as the intrinsic detector's efficiency is known (Giaugue *et al.*, 1973).

3.1. EXTRACTION TECHNIQUE

We have compared four different extraction techniques with ion-exchange resin loaded filter papers: passage of the solution through the filter with aid of a peristaltic pump; with aid of an hour glass system; by dropping it on a separatory funnel; and by bathing the filter in the solution.

The first filtration technique permits a rapid flow of the solution through the filter and presents several advantages when using a peristaltic pump with several tubes in parallel, but it does not allow, without considerable difficulty, the passage velocity of the solution to be varied continuously. This technique cannot be used for filtering very small quantities of solution (few ml) and it introduces some perturbation in the circuit.

The second technique has the advantage of using both faces of the filter to obtain a very homogeneous deposit, but it is unsuitable for variable volumes of solution and does not allow the passage velocity of the solution to be varied.

The third technique consists of passing the solution through the filter using a dropping procedure which allows the passage velocity of the solution and the volume of the solution to be varied with ease. It furthermore permits the control of the collection of ions at any passage of solution, and to attain sufficiently homogeneous deposit of the filter as long as one takes care to create a large flow so that the filter is

completely bathed. The filtration velocity in such case must be of about 10 ml of solution min^{-1} .

The bathing technique has been used with granular resins with good results, and works very well for very small quantities of solution. For a complete ionic capture with resin filter papers this filtration technique requires on the other hand rather long intervals of time. In the case of biological liquids where filtering of more than a few ml of liquids is not possible, the immersion of a filter in the liquid allows an almost complete trapping of the ions.

Once the filtration technique was selected, the following optimization steps were carried out:

3.1.1. *Choosing the number of Filtrations*

It is necessary to obtain almost complete extraction of the ions from the solution. It has been experimentally determined that with 6 to 14 passages the filter collects 85 to 95% of the ions. If a homogeneous deposit is desired, particularly for light elements XRF analysis, it is necessary to alternate the filtering on the two faces of the filter.

3.1.2. *Choosing the Optimal Filtration Volume*

The exchanging capacity of a filter is 0.2 meq for cationic resins and 0.15 meq for anionic ones. This corresponds to an ionic trapping which is for example 4 mg for the Ca^{2+} ions. Therefore the filter runs out of its exchange capacity for a larger amount of filtered elements. For the maximum trapping of ions having a much smaller concentration than Ca, for example concentration of the order of parts per million or less, the optimum volume to be filtered is the maximum one relative to the majority ion present in the solution. For example in Figure 1 are shown the Sr (0.14 ppm) and Zn (0.04 ppm) counts versus the filtered volume in the case of 'Fiuggi' mineral water, where a volume of about 300 ml is sufficient to saturate the Ca content.

3.1.3. *Choosing the pH of the Solution*

The optimum capturing zone of the filter of the SA-2 type in relation to the pH of the solution is for $\text{pH} < 4$. This has been verified employing standard solutions of Cu^{2+} and varying the acidity. In fact there is an optimum trapping for $\text{pH} \approx 3$. A different behavior, on the other hand is obtained with standard solutions of Mn^{2+} . In this case the capturing follows rather a constant function with no dependence by pH up to $\text{pH} = 7$. In our case water samples were filtered at $\text{pH} \approx 4$.

3.2. ABSOLUTE DETERMINATION OF THE CONCENTRATION

The following conditions must be fulfilled in order to achieve an absolute determination of the concentration of the ions in the solution to be filtered:

- that the filter must collect at least 90 to 95% of the ions of the solution. This condition can be controlled by analyzing successive filters containing the residual

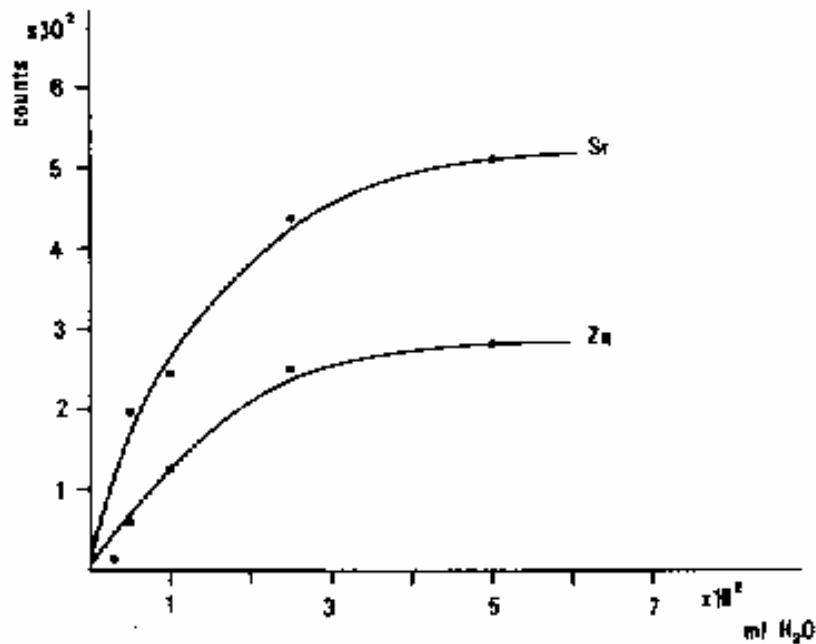


Fig. 1. Strontium and Zn counts versus the filtered volume of 'Fiuggi' water.

ions of the already filtered solution. An example is shown in Figure 2. In any case with a sufficient number of passes the ions in solution can be almost completely collected;

- that the distribution of the ions on the filter be approximately uniform. This condition has been tested for many cases and for different elements, enabling us to determine a minimum decrement of the counts from the center to the border of the filter;

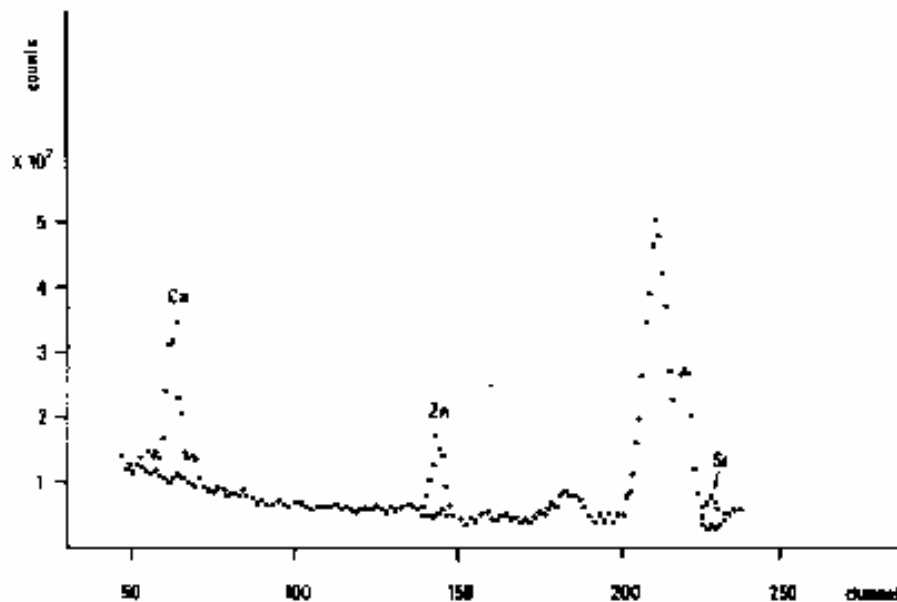


Fig. 2. XRF spectrum of 25 ml of tap water after 8 passes through an ion exchange resin loaded filter (upper curve) and after successive 8 passes through a second filter (lower curve).

- that there be a linear relation between the concentration of the analyzed ions and the relative counts. This condition is of particular importance and has been verified with standard solutions of various concentrations and for various ionic forms. It was found to be satisfactory as long as the saturation condition of the filter was not reached (Figure 3);

- that it is verified that the sample is thin in order to employ the linear relation (1). This hypothesis is verified when the condition:

$$m(\mu(E_1) + \mu(E_2)) \ll 1 \quad (2)$$

holds, or with optimum approximation, when $m(\mu(E_1) + \mu(E_2)) = 0.05$. For the maximum deposit on the filter, this approximation yields the values shown in Figure 4.

When the absorption of the X-rays by the analyzed element by the filter is taken into account, Equation (1) can be written:

$$N_i \approx N_0 K \epsilon(E_2) \omega_i \mu_{f,i} (1 - 1/J_i) e^{-\mu(E_2)x} C_i m \text{ counts } s^{-1} \quad (1')$$

The intrinsic efficiency of the detector for the fluorescent X-rays of energy E_2 is 100% in the energy range from 5 to 18 keV. For lower energies it is 96% for Ca X-rays, 93% for K X-rays and 86% for Cl X-rays.

The values of ω_i are listed in Bambynek *et al.* (1972) and so are the values of J_i (Clark, 1974) and $\mu_{f,i}$ (McMaster *et al.*, 1969). For this latter parameter it must be noted that the photoelectric effect due to the contribution of the X_1 lines of uranium, for the Pu^{238} source, that is $L_\alpha = 13.5$ keV (relative intensity 35%), $L_\beta = 16.8$ keV (r.i. 53%) and $L_\gamma = 20.2$ keV (r.i. 13%) can be approximated with as if there is a single line at 16 keV.

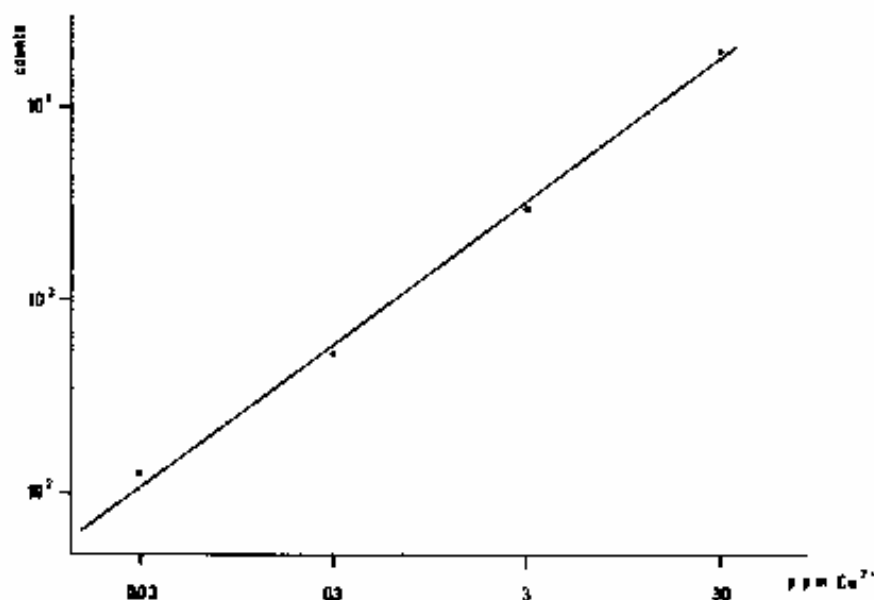


Fig. 3. Calibration curve for the determination of the Cu^{2+} ions content in water solution collected on SA-2 resin loaded filters.

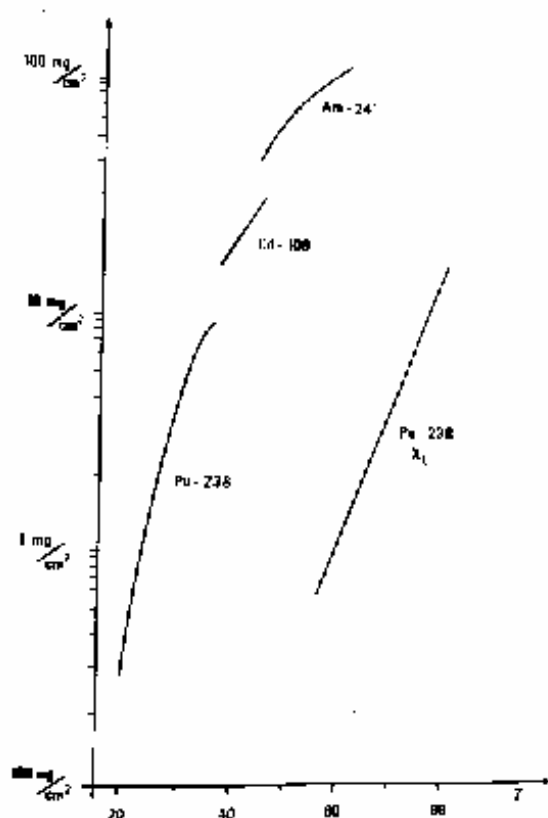


Fig. 4. Mass per unit area of elements satisfying the thin specimen condition $m(\mu(E_1) - \mu(E_2)) = 0.05$ as a function of atomic number Z and of the exciting source.

Finally, standard samples constituted by variable quantities of Co (from 1 to $200 \mu\text{g cm}^{-2}$) and of Cu (from 10 to $150 \mu\text{g cm}^{-2}$) were used. From the counts obtained with these standards using constant geometry, we have obtained the value of N_0K .

3.3. MINIMUM DETECTION LIMITS

The minimum detection limit of the technique depends critically on the concentration of the major ions present in the water analyzed (generally Ca), the radioisotopic source, the detector and the measuring time. Using the semiconductor detectors described, and the Pu^{238} and Am^{241} sources, the approximate minimum detection limits in a measuring time of 4000 s are given in Table IV.

3.4. CALCIUM ANALYSIS OF WATERS

The analysis of Ca content in different waters was carried out using the simple instrumentation described in Section 2, which had a $2 \text{ Ci } \text{H}^{137}\text{Zr}$ radioisotopic source and a thin window Xe gas proportional counter. The results, obtained during 100 s, are plotted in Figure 5 and are compared in Table V to the results obtained with

TABLE IV

Approximative MDL (in ppb) of the XRF technique using ion exchange resin loaded filter papers; measuring time: 4000 s

Ca	200-500	Sr	30-100
Tl	50-200	Cd	15-50
Mn	7-30	Ba	10-30
Fe	5-15	Pb	20-60
Cu	3-10		
Zn	2-6		
Br	1.5-5		

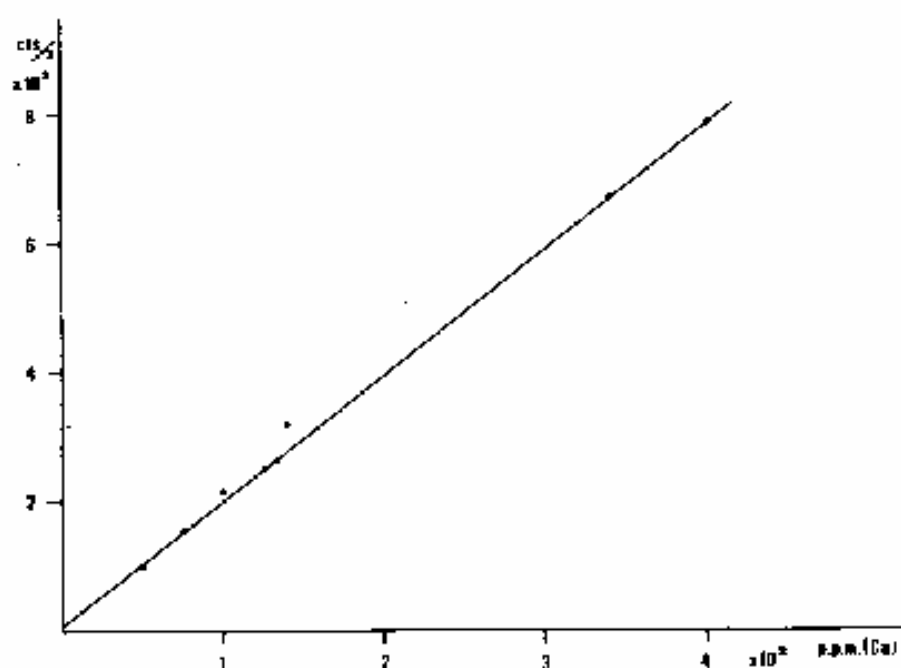


Fig. 5. Calibration curve of the Ca ions concentration in different kinds of water. Radioisotopic source: $H^{90}Zr$ (2 Ci). Measuring time: 100 s.

TABLE V

Analysis of Ca in different waters employing the XRF technique and traditional methods

Water	Ca content (in ppm) with the XRF technique	Ca content (in ppm) with traditional methods
Fuggi	7	13
La Rocchetta	42	50
Nepi	75	75
Egeria	107	100
Peschiera	161	—
Appia	157	140
Sangemini	337	340
Ferrarelle	396	400

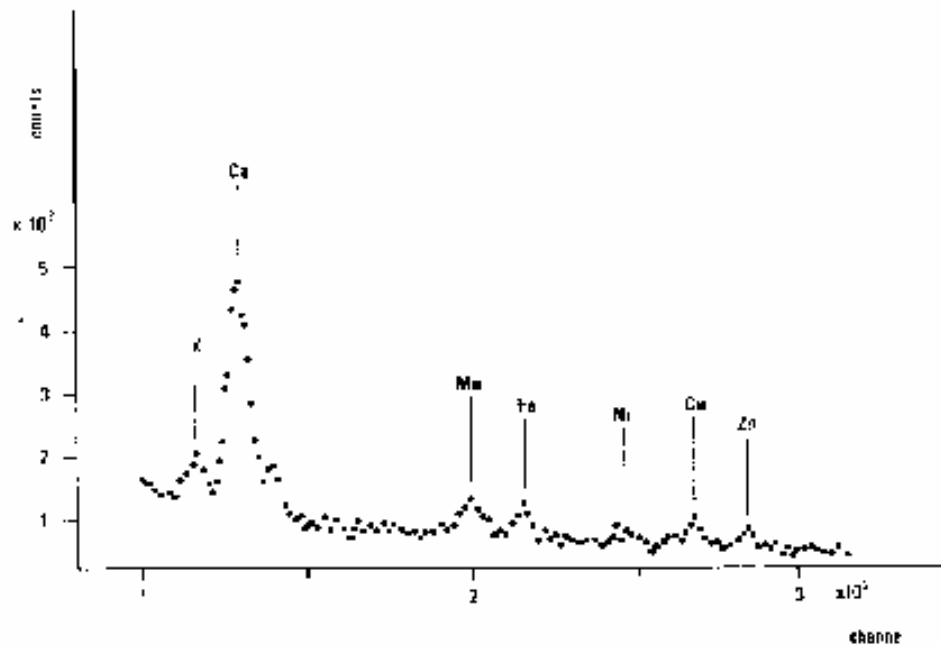


Fig. 6. XRF spectrum of 250 ml of 'Piuggi' mineral water collected on a SA-2 filter. Radioisotopic source: Pu^{238} (10 mCi). Measuring time: 4000 s.

traditional methods. It can be observed that the average deviation between XRF analysis and the results of the other analyses is about 7%. A little difference can be obtained between the counts on the two faces of the same filter because of self-absorption of Ca X-rays by the filter itself. This effect requires measuring both faces separately and assuming an average value of counts.

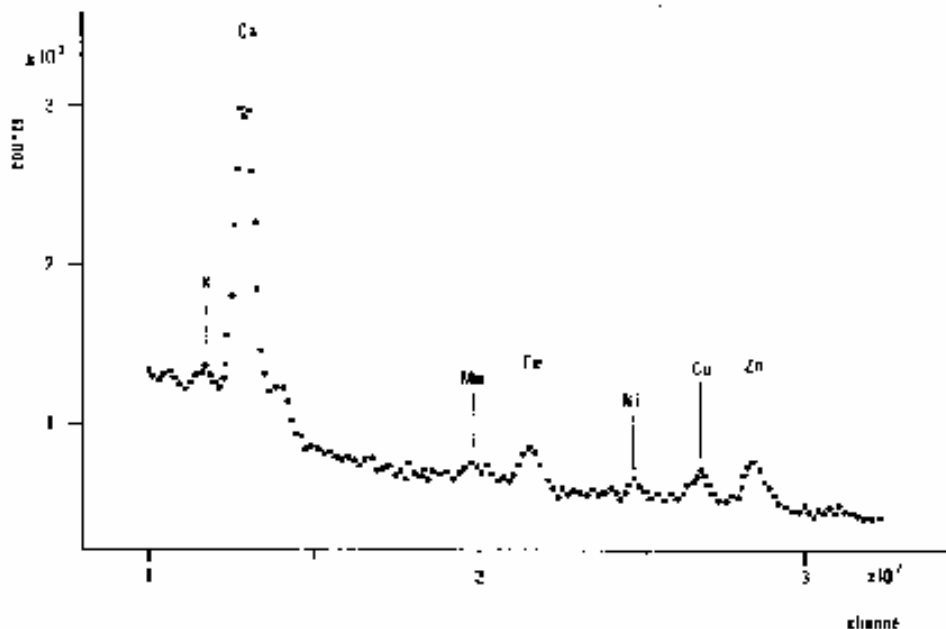


Fig. 7. XRF spectrum of 50 ml of 'Nepi' mineral water collected on a SA 2 filter. Radioisotopic source: Pu^{238} (10 mCi). Measuring time: 4000 s.

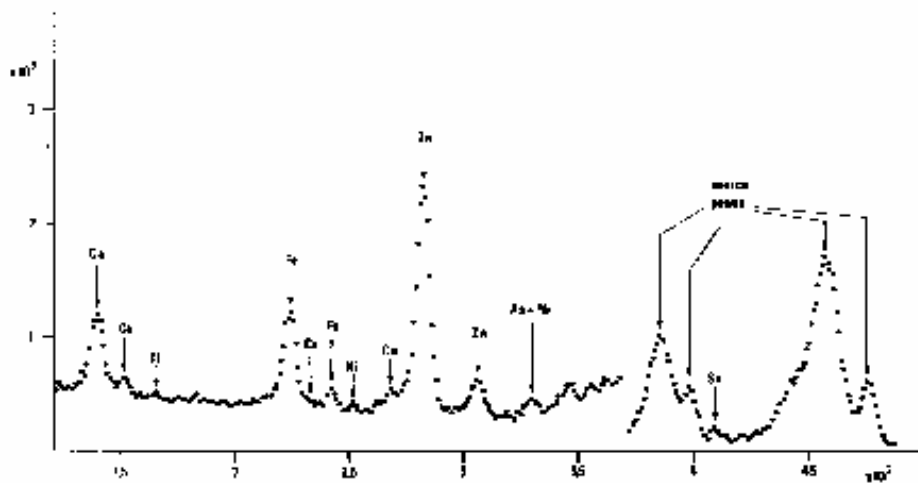


Fig. 8. XRF spectrum of 500 ml of tap water collected on a SA-2 filter. Radioisotopic source: Pu^{239} (10 mCi). Measuring time: 4000 s.

3.5. MULTIELEMENT ANALYSIS OF WATERS

For contemporaneous multielement analysis of waters, semiconductor detectors have been used. Figures 6 to 9 show spectra of mineral and tap water samples. The results obtained for samples of mineral and tap water are summarized in Table VI and compared to the available results of analyses carried out with other methods (chemical analysis, atomic absorption, colorimetric methods etc.). As can be noted, the agreement is generally good.

TABLE VI

Quantitative results for different water samples by XRF analysis and by traditional methods (in parentheses). Concentration in ppm

Element	Water				
	Nepi*	Egeria*	Fiuggi*	Appia*	Peschiera**
K	43	65 (73)	2.2 (3)	55 (68)	—
Ca	75 (75)	95 (100)	14 (13)	130 (140)	140
Mn	0.6 (0.5)	0.3	0.04	0.07	—
Fe	0.2 (0.18)	0.1	0.05	—	0.9
Co	—	0.05	—	—	0.05
Ni	0.08	0.06	0.015	0.03	0.03
Cu	0.03 (0.03)	—	0.007	—	0.06
Zn	0.03	—	0.04	—	1.0
As	—	—	—	—	0.03
Sr	0.6 (0.5)	1.1	0.1 (0.1)	1.3 (2)	0.4
Cd	—	—	0.15	—	0.03
Si	—	0.07	0.1	0.06	0.06
Sb	—	—	—	—	0.01
Ba	0.05	0.4	0.08	0.4	0.9
Pb	—	—	—	—	0.03

*Mineral water

**Tap water

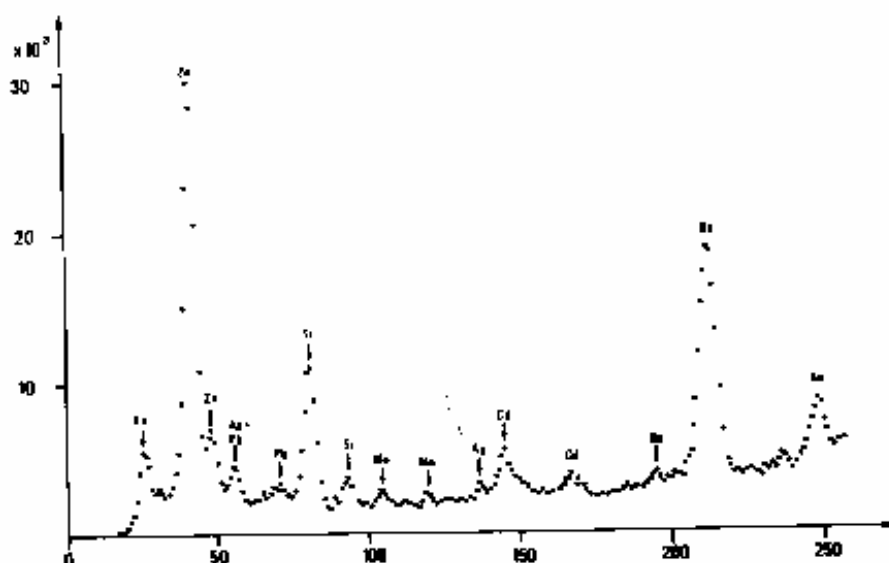


Fig. 9. XRF spectrum of 500 ml of tap water collected on a SA-2 filter. Radioisotopic source: Am^{241} (50 μCi). Measuring time: 10^4 s.

3.6. EVALUATION OF THE ERRORS

A correct evaluation of the error in the determination of trace element concentration in waters is difficult because of the variety of their origin. It may in fact depend on the following reasons: errors due to the use of standard samples and to the computation of the parameters of Equation (2'); counting statistics; errors due to incorrect use of extraction technique; inhomogeneity of the collection in the filter etc. By analyzing these various sources of error it can be surmised that the error due to counting statistics and or due to the employment of standard samples and to Equation (2') ranges around 20%. An incorrect use of the filtration technique can lead to errors which can be very much larger.

4. Conclusion

A multielement analytical technique based on the radioisotopic X-ray fluorescence has been developed and applied to the studies of natural waters. A rapid pre-enrichment step utilizing ion exchange resins loaded papers, followed by X-ray analysis of the filter paper permits the simultaneous measurements of a large number of trace constituents. Samples of mineral water and of tap water were analyzed.

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