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FLAME EMISSION SCANNING AS AN ANALYTICAL TOOL IN GEOCHEMICAL STUDIES OF ALKALI METALS

RIASSUNTO. — Nell'ultimo decennio le tecniche analitiche basate sulla spettrofotometria dell'emissione di fiamma sono state progressivamente sostituite dai metodi basati sull'assorbimento atomico. Questo trend è riscontrabile anche nell'analisi degli alcalini, sebbene questi presentino caratteristiche molto favorevoli per la loro determinazione mediante emissione di fiamma.

Comunque, proprio le strumentazioni attualmente disponibili per l'assorbimento atomico hanno fornito apparecchiature adatte all'effettuazione di analisi mediante scansione dell'emissione di fiamma, ed hanno quindi direttamente riproposto la validità di quest'ultima tecnica.

Nella presente nota vengono discussi i risultati metodologici conseguiti mediante scansione dell'emissione di fiamma nelle analisi geochimiche degli alcalini. Le sensibilità ottenute con l'impiego dello spettrofotometro Perkin-Elmer 303 sono le seguenti, espresse in microgrammi per litro:

Na 0,05 K 5 Li 0,1 Rb 25 Cs 200.

Nel lavoro vengono discusse le caratteristiche delle determinazioni basate sull'emissione di fiamma, sia mediante scansione che senza, con particolare riferimento all'analisi del litio.

Pregio essenziale dell'analisi condotta mediante scansione risulta essere una specificità eccezionalmente elevata che consegue da un tipo di misura concettualmente simile a quella spettrografica. Per il Li, Na e K ciò è accompagnato da una sensibilità molto elevata. Per questi elementi è pertanto possibile effettuare analisi geochimiche di qualità molto elevata.

ABSTRACT. — In the last decade, flame emission photometry has been progressively substituted by atomic absorption in the analysis of alkali metals. But, at the same time, the instruments available for atomic absorption have furnished a suitable tool for trace analysis of these elements by the scanning of flame emission.

The results obtained on applying flame emission spectrophotometry and the peculiar characteristics of this analytical method are discussed in the present

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paper. The sensitivity achieved with the Perkin-Elmer 303 spectrophotometer for the five alkali metals is, in micrograms per litre, as follows:

Na 0.05 K 5 Li 0.1 Rb 25 Cs 200.

Flame emission analysis has been studied, and applied, with scanning as well as without it. We would like to stress first of all the high sensitivity obtained for Na, Li, and K. Flame emission scanning is, moreover, highly specific; it is, from a phenomenological viewpoint, quite similar to spectrography.

The records in Fig. 5 show the high value of the background/signal ratio we met in the analysis of geochemical samples. These records stress how a reliable analysis can be performed only by scanning. The results of lithium analysis of four U.S.G.S. Standard Rocks are also reported.

The sensitivity and specificity of the method enable us to carry out high-quality Li analysis down to $0.1 \mu\text{g}/\text{l}$ in solution, which corresponds to $0.x \text{ ppm}$ in solid sample; this covers any kind of analytical needs in geochemistry.

1. - Introduction.

In the last decade flame emission technique has been gradually disregarded as an analytical tool. This trend is evident in the analysis of alkali metals too, though these elements display highly positive emission characteristics.

Flame emission technique was gradually substituted by atomic absorption methods, for the following reasons.

a) Atomic absorption measurements furnish — generally speaking — high quality results because of the low interference from other elements and/or compounds, and because of the high accuracy that can be obtained when the concentration of the element tested for falls within the optimum detection range.

b) Atomic absorption methods can be applied to a much wider range of elements.

c) Commercial atomic absorption instruments are highly reliable and their well designed optional accessories can greatly increase the performance of the basic instrument as regards the quality of the eventual analytical results, the range of applicability of the method, as well as their productivity in routine work.

Beside all these positive factors, a few limiting aspects intrinsic to atomic absorption measurements must be stressed too. Atomic

absorption measurements are usually carried out by comparing the intensity of the absorbed light with the intensity of the source.

When incident and absorbed fluxes are very similar, the measurement suffers from low accuracy. The real sensitivity of the A.A. method is, in fact, intrinsically limited by the difficulty of obtaining reliable physical measurements of very small differences in light intensity (approx. 10^{-3}) and, moreover, by the difficulty of deriving the presence and concentration of the element under investigation from such small differences, since other physico-chemical processes can cause changes of the same order of magnitude.

Emission photometry is characterized instead by the direct proportionality between concentration and radiation intensity. This characteristic can result in a much higher sensitivity and in a wider working range of concentrations, and both of these characteristics are of essential importance in geochemical analyses.

In fact, the sensitivity of the A.A. technique for lithium, rubidium, and caesium is often too low with respect to the content of these elements in many kinds of natural substances (fresh and sea water, some types of rocks like evaporites, etc.).

For this reason, a systematic study was undertaken with the purpose of critically evaluating the perspectives offered by the application of flame emission spectrophotometry, with and without scanning, to the geochemical analysis of alkali metals.

It is to be noted particularly that the accessories of up to date commercial A.A. instruments provide quite suitable tools for flame emission analysis. In the present study a Mod. 303 Perkin-Elmer spectrophotometer was used, fitted with the accessories for emission.

We deal here with the results of the methodological study, with particular reference to the analysis of lithium. This element is in fact of great geochemical interest; moreover the results obtained for this element give some indication as to the possibilities of analyzing caesium and rubidium too.

2. - The Analysis of Alkali Metals by Flame Emission.

The range of possibilities of the equipment we have, was tested for Na, K, Li, Rb, and Cs. In Fig. 1 are shown the recorder tracings obtained, by scanning, for the alkali metals. An acetylene-air flame and a 10 cm burner were used.

We point out first of all the sensitivities obtained, which are shown in Table 1 in comparison with the sensitivities of atomic absorption. It turns out that emission photometry clearly offers much higher sensitivity as far as sodium and lithium are concerned, though less so for potassium. Without going too much into detail on the

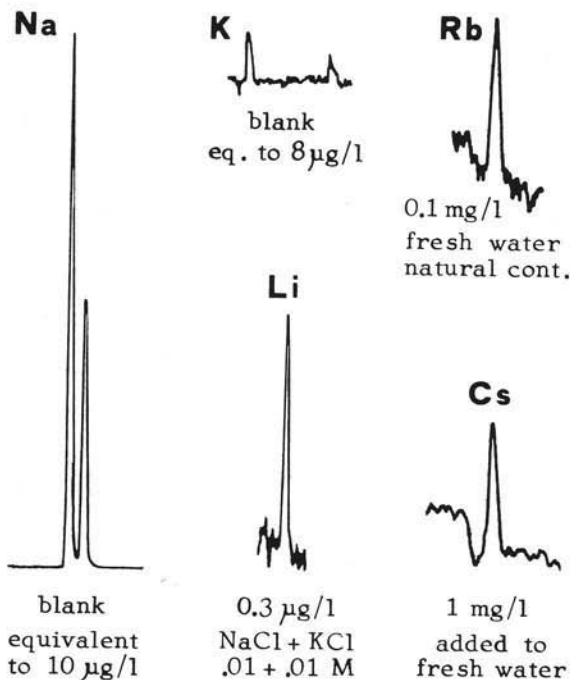


Fig. 1. — Records showing the emission scanning of the analytical lines of the alkali metals, starting from low level solutions.

working meaning given to the term «detection limit» in the area of atomic absorption techniques, we have to point out that the sensitivity of the flame emission scanning is indicated by us as the concentration yet detectable with the necessary specificity.

As shown in the records of Fig. 1, the very high sensitivity of sodium and potassium detection is of no practical use, due to the widespread contamination of these two elements. The sodium and po-

TABLE 1. — *Sensitivities of Alkali Metal Analysis by Flame Emission Scanning and Atomic Absorption (micrograms per litre).*

	Na	K	Li	Rb	Cs
	5890	7665	6708	7800	8521
Flame Emission Scanning	0.05	5	0.1	25	200
Atomic Absorption	for 1% Abs.	40	100	200	500
	Det. Limit	4	5	5	50

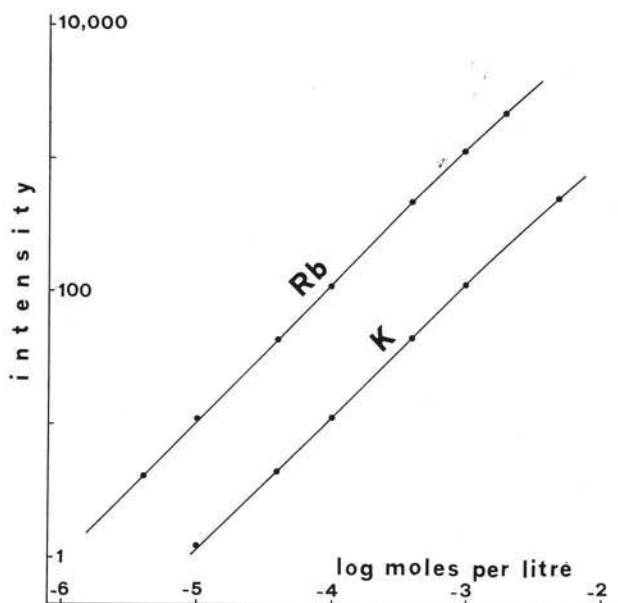


Fig. 2. — Flame emission calibration curves for Rb and K obtained without scanning, starting from solutions with low content of interfering cations.

tassium contained in air and/or in acetylene cause an emission approx. equal to the emission of a 10 ppb solution.

Fig. 2 shows the emission-concentration curves for aqueous solutions (pH \sim 1) of potassium and rubidium, obtained without scanning.

These calibration curves were utilized in numerous analyses of these elements in the concentration range from 10^{-6} to 10^{-2} M.

These curves point out one of the positive characteristics of emission analysis, that is the possibility of carrying out good quality analyses over a very wide range of concentrations using only one analytical line.

3. - Analysis of Lithium.

As already mentioned, our methodological studies were focused on the analysis of lithium. A better knowledge of the distribution and circulation of this element is of great geochemical interest. The ionic and crystallochemical features of this element are in fact quite peculiar. Its small ionic radius (0.68 \AA as compared with 0.97 for Na, 1.33 for K, 1.47 for Rb, and 1.67 for Cs), makes it impossible for lithium itself to enter the lattice structure of the minerals of other alkali metals.

Among the major elements, the only ones that show an ionic radius similar to lithium are Mg and Fe, but the difference in the ionic charge — and in ionic potential (Z/r) — tends to restrict the geochemical analogies between lithium and these elements.

In the supergene environment, lithium can enter the lattice structure of clay minerals, but secondary minerals of lithium with low solubility do not exist.

The overall resulting behaviour of lithium is characterized by a high geochemical mobility.

Even if the geochemistry of lithium is known in its essential aspects, the lack of analytical methods of high sensitivity has limited up to now the extending of our knowledge to specific geochemical processes such as, e.g., the leaching of lithium by fresh water and the distribution of lithium between precipitates and solutions in evaporitic processes.

The analytical method presented here has been widely used in studying the geochemical behaviour of lithium in the above natural processes, and the results obtained will be discussed in separate papers.

Fig. 3 shows the emission-concentration curves we got without scanning. The figure shows both the curve obtained with a 10 cm

flame (the same burner used in atomic absorption placed along the optical axis of the instrument) as well as the curve obtained with a burner arranged perpendicular to the optical axis. For convenience of representation, the values of intensities corresponding to the straight line parts of the curves have been equalized for the same concentrations.

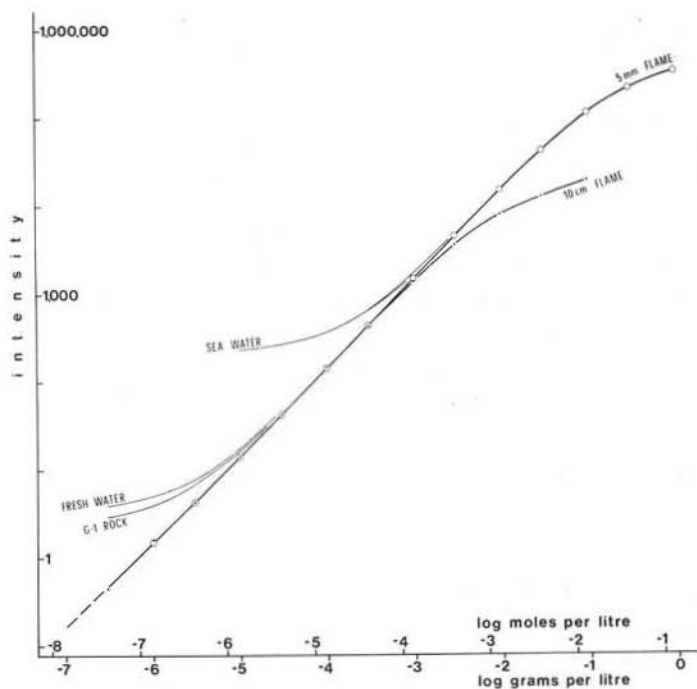


Fig. 3. — Intensity-concentration relations for the determination of Lithium without scanning.

The foot-like curves on the left indicate the interference effect induced by representative natural matrices.

The area between the straight line and each «foot» indicates the uncertainty of the analytical results starting from this kind of matrix (see text).

The narrower flame curve shows the bending caused by self-absorption at concentrations higher than those at which the analogous inflection takes place with a longer flame.

Each of the curves given shows how it is possible to work in a concentration range of 5 or 6 decimal orders without falling into angular coefficients so low as to spoil the measurement by too much uncertainty. Both of the curves were obtained from aqueous solutions (0.1-N HCl) which contained *only* lithium as a cation.

In reality, geochemical studies require the analysis of complex and widely varying matrices, where lithium, moreover, can be present at trace or ultratrace level. In other words, it often happens that substances are to be analyzed that show an emission caused by other elements, of an intensity sufficient to spoil the specificity of the measurement. All other conditions being equal, this kind of interference depends on the bandwidth.

Bandwidth is one of the most important parameters with regard to the goal of the overall quality obtainable. This parameter in fact conditions the line to background ratio. It would be therefore convenient to narrow the band, but the low stability of the monochromator alignment for instruments of this class hinders, in practice, the use of a very low bandwidth.

We must remember that high-performance direct-reading spectrographic equipment are specifically designed to guarantee this alignment (e.g., thermostating the equipment), and therefore to minimize the bandwidth and get a high signal to background ratio.

In the analyses carried out without scanning, the best compromise between the contrasting requirements above cited was obtained with a 13 Å bandpass, taking into account the observed drift of the monochromator during short runs.

In Fig. 3 is also shown the behaviour of measurements resulting from analyses of representative natural matrices, that is, sea water, a sample of fresh water from the Latium Region, and the solution obtained from perchloric-hydrofluoric acid attack of a U.S.G.S. standard rock. At low concentration, a large fraction of the measured intensity is matrix emission in the 13 Å-wide band. It shows up as a «foot» in the left side of the curve because of the logarithmic scale.

The reliability of the analyses turns out to depend on the ratio of lithium emission to the emission of other cations. The experiments performed indicate that calcium and sodium are the elements which cause the most interference.

Fig. 4 shows the lithium emission-concentration curve obtained *by scanning*, starting from a solution of 0.01 M NaCl + 0.01 M KCl + 0.1 N HCl.

By scanning analysis it is possible to clearly cut out the background emission and to obtain a precise measurement of the intensity

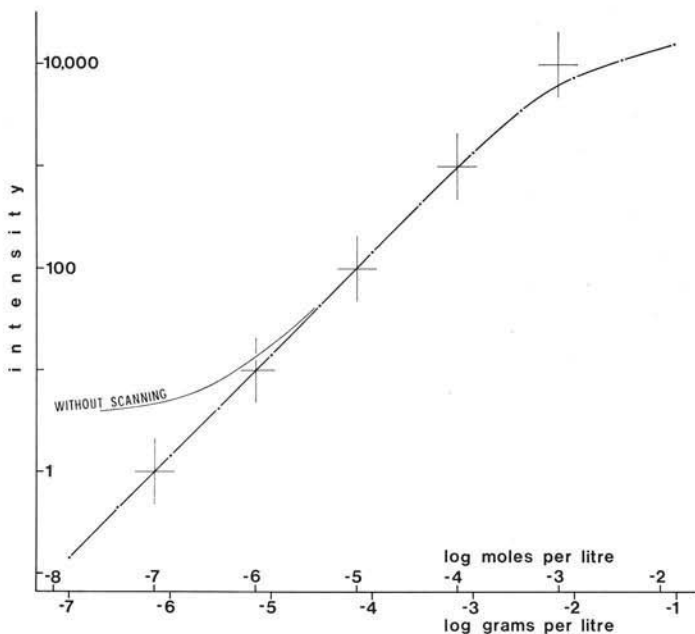


Fig. 4. — Intensity-concentration relation of flame emission scanning analysis of Lithium (10 cm flame).

of the analytical line. A comparison with the curves of Fig. 3 shows that the analysis by scanning enable us to detect lower lithium concentrations, with in addition a higher specificity. It can be pointed out that the emission due to sodium and to potassium in the concentrations used, would otherwise appear to be due to $3 \mu\text{g}/\text{l}$ of lithium in the solution.

Notice the value, which exactly equals 1, of the slope of the straight line part of the curve. This is also due to the buffering effect of sodium and potassium on the ionization of lithium.

4. - Lithium Analysis of Geochemical Samples.

Aside from the need to discriminate between the emission of the analytical line and the background emission, it should be kept in mind that, for a given concentration of the element under examination, emission intensity depends on the physico-chemical conditions of the source. Among the most important factors can be mentioned the temperature of the flame itself and the influence of alkali metals on ionization, and thus on emission.

We have not studied the effect of other different flames, given the satisfactory results obtained with the acetylene-air flame.

We did study however how the presence of sodium, potassium, and sodium + potassium influences lithium emission. The concentrations of sodium and potassium examined cover two decimal orders, viz. from 10^{-3} to 10^{-1} M, while lithium concentration was kept constant at 10^{-5} M. The results obtained show that the effects on the yield are in the order of magnitude of 5%.

The variation coefficient of repeated trials by scanning turns out to be around 3%.

Lithium was analyzed, by scanning, in the U.S.G.S. standard rocks with the lowest lithium content (< 2 ppm); for this reason there were no recommended nor retained values. The rocks analyzed belong to the second series prepared by the U.S.G.S., and are DTS-1 and PCC-1. In addition, G-1 and W-1 were analyzed. The values 22 and 14.5 respectively are « retained » for these rocks (Flanagan, 1973).

TABLE 2. — *Lithium Analysis of U.S.G.S. Standard Rocks (ppm).*

DTS-1	1.8	PCC-1	1.1	G-1	22	W-1	12
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The data shown in Table 2 are the averages of the values obtained from decompositions repeated two or three times. The sample was decomposed by sintering with sodium peroxide, and the sintered mass was dissolved in 3M-HCl. This type of attack has proved to be highly reliable, both as regards the efficiency of the decomposition itself, and because the sodium peroxide has a low lithium content, i.e. less than

0.01 ppm; the interference from sodium is in turn eliminated by scanning. The original records are shown in Fig. 5.

In the same figure is shown the record for the analysis of a halite sample, from Sicily (serie Gessoso Solfifera). This sequence was studied in detail for the distribution of lithium.

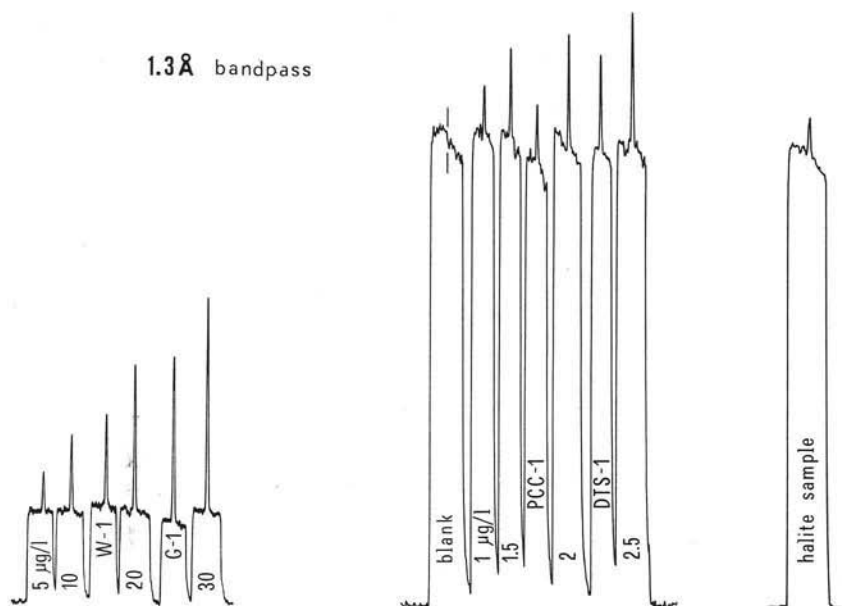


Fig. 5. — Records obtained under unfavorable conditions because of a high Na/Li ratio.

The U.S.G.S. standard rocks have been attacked by sintering with Na_2O_2 , and the halite sample has been dissolved in dilute HCl.

Notice the high background to signal ratio of this latter sample, that hinders the Lithium detection without scanning.

The record obtained from the halite sample, in particular, points out the characteristic advantages of an analysis performed by scanning.

These advantages can be summarized as very high specificity and sensitivity, even better from an overall point of view than for spectrography.

The analytical sensitivities for caesium and rubidium can be greatly improved, in our opinion, with the use of a red sensitive photomultiplier.

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