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SHORT COMMUNICATIONS

Automatic determination of calcium and magnesium in water

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THE INDIVIDUAL determination of calcium and magnesium in water is very often more useful than a total hardness determination, both from the point of view of the maximum allowed concentration of magnesium in drinking water, and of the different effects of the two metals on the corrosion of metal pipes.

As far as we know the methods reported for the automatic colorimetric determination of calcium or of magnesium[1-6] are based on recording the absorbance at a suitable wavelength according to the specific reagent employed for each element, under different experimental conditions. In this paper a method is described for the automatic determination of both these elements with the same complexing agent and measurement of the absorbance at the same wavelength, with changes in the amounts of other complexing agents added to the solution.

The metallochromic agent, Eriochrome Black T (EBT), was chosen for its stability over long periods of time and its low cost. The Menon and Das procedure[7] was used, slightly modified and adapted for automation. EBT forms coloured complexes with both calcium and magnesium, but the absorptivity for magnesium is always much greater than that for calcium at the same pH and wavelength.

Menon, using solutions buffered at pH 9·5, measured the decrease in absorbance at 650 nm as a function of magnesium concentration, considering the calcium contribution to the absorbance at this wavelength to be negligible. On addition of MgEDTA to the solution all the calcium initially present as CaEBT complex was quantitatively converted into CaEDTA, and the equivalent amount of magnesium, displaced from the EDTA complex, formed MgEBT. From the difference in absorbance before and after addition of MgEDTA, the concentrations of both metals were obtained by successive approximations.

In our case we have measured at 571 nm, where an isosbestic point is observed for CaEBT and EBT. It is evident that under these conditions all the variations in absorbance are really proportional to the initial magnesium concentration, regardless of the amount of calcium in the solution.

Over the ranges 3–25 ppm of magnesium and 5–40 ppm of calcium the accuracy for both the elements was ±4%—better than the corresponding accuracy obtained by the manual method, which is about ±10%.[7]

PRINCIPLE OF THE METHOD

In Figs. 1*a* and 1*b* are shown some spectra of solutions containing EBT and calcium or magnesium respectively, at different concentrations. From these spectra isosbestic points for CaEBT and EBT at 571 nm and for MgEBT and EBT at 578 nm can be seen. In principle it would be possible to determine the former at 578 nm and the latter at 571 nm, avoiding any interference. From a practical point of view, however, this is to be disregarded owing to the very poor sensitivity for calcium at the magnesium isosbestic point and to the fact that measuring at two different wavelengths would require two spectrophotometers or the continual repositioning of the monochromator in a single instrument.

Using the same dye concentration in both the reference and sample cells, we have at any prefixed wavelength:

$$A = C_{Mg}(\varepsilon_{Mg} - f\varepsilon_I) + C_{Ca}(\varepsilon_{Ca} - f'\varepsilon_I) \quad (1)$$

where f and f', depending on the pH,[8-9] represent the number of complexing agent molecules bound to each magnesium or calcium ion respectively. A is the total absorbance, C the concentration, and ε the molar absorptivity of the species indicated by the subscript (I represents EBT, Ca and Mg represent CaEBT and MgEBT). Under our experimental conditions (pH = 10) it is very likely that f and f' are equal to unity.[10] At 571 nm

$$\varepsilon_{Ca} = f'\varepsilon_I \text{ and } A = C_{Mg}(\varepsilon_{Mg} - f\varepsilon_I) \quad (1a)$$

We have found that equation (1*a*) holds for any excess of calcium as long as the concentration of free EBT allows magnesium to be present only as the MgEBT complex. Once the magnesium concentration has been determined, calcium is quantitatively displaced from the dye complex by addition of MgEDTA, according to:

$$\text{CaEBT} + \text{MgEDTA} \rightarrow \text{CaEDTA} + \text{MgEBT} \quad (2)$$

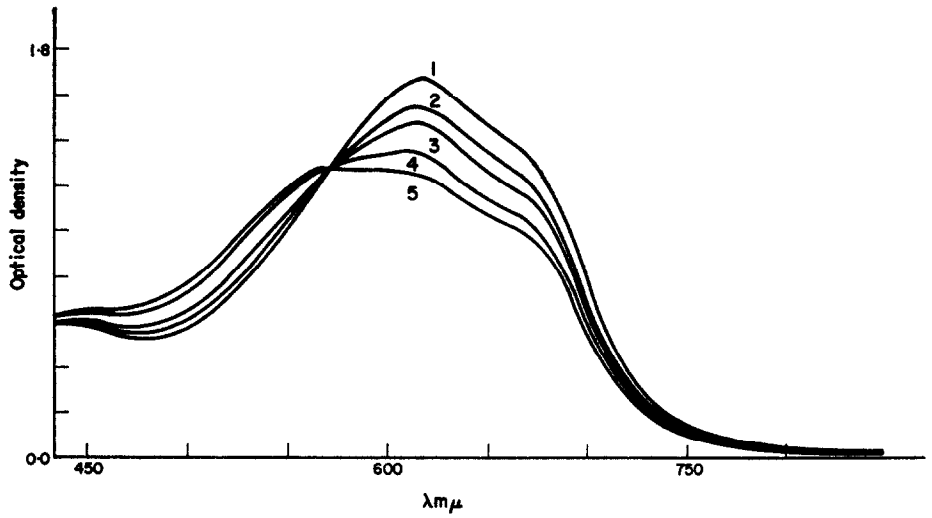

FIG. 1*a*.—Absorption spectra of EBT and CaEBT complex at pH 10.
EBT 0·144 × $10^{-3}M$ for all the curves.
* Ca: 0 ppm, curve 1; 10 ppm, curve 2; 20 ppm, curve 3; 40 ppm, curve 4; 50 ppm, curve 5.

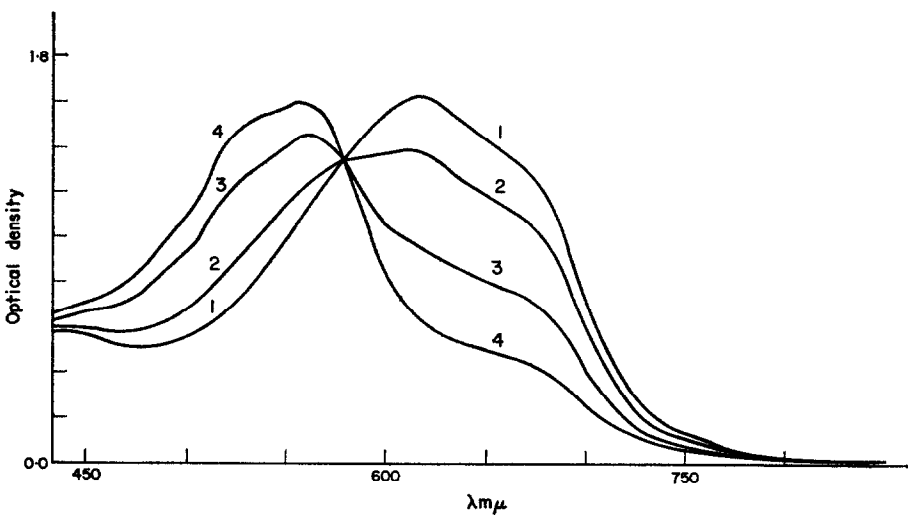

FIG. 1*b*.—Absorption spectra of EBT and MgEBT complex at pH 10.
EBT 0 144 × $10^{-3}M$ for all the curves.
* Mg: 0 ppm, curve 1; 2 ppm, curve 2; 6 ppm, curve 3; 10 ppm, curve 4.

By measurement of the increase in absorbance corresponding to the MgEBT obtained by this reaction, the concentration of calcium (in ppm) may be obtained with the same degree of accuracy as that of magnesium and with an amplification factor, with respect to its direct measurement at any wavelength with the exception of 571 nm, equal to: $\frac{\varepsilon_{Mg} - \varepsilon_I}{\varepsilon_{Ca} - \varepsilon_I}$.

Heavy metals, if present, affect to different extents the determination of magnesium and calcium. In the first case for instance, the presence of Cu(II) or Fe(II) causes a decrease in absorbance ($\varepsilon_I > \varepsilon_{CuI}$)

* All the concentrations reported are referred to the original concentration in the samples. The actual concentration in the optical cell was in each case 8 times more dilute.

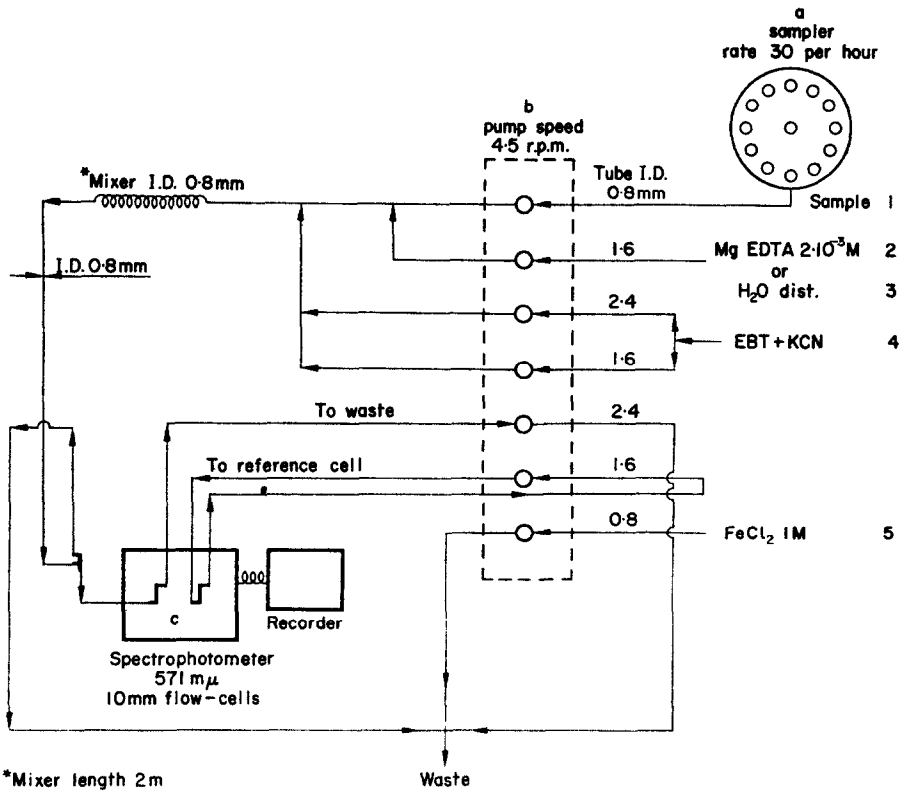

FIG. 2.—Diagram of automatic analyser.

which counteracts the increase due to magnesium, whereas Zn(II) has very little effect on measurements at 571 nm ($\varepsilon_{EBT} \sim \varepsilon_{ZnEBT}$) and so on. In the second case, on addition of MgEDTA, only Zn(II) displaces magnesium from MgEDTA, increasing the absorbance, while Cu(II) and Fe(II) still form the more stable CuEBT and FeEBT respectively.[11] For this reason, their presence must be masked by addition of cyanide to the solution to form the very stable cyano-complexes, which are stronger than the corresponding complexes with EBT or EDTA. The excess of cyanide can be removed afterwards by adding the waste solution to 1*M* $FeCl_2$ solution (see Fig. 2).

The choice of pH 10 as working condition is a compromise between the maximum formation of MgEBT and the minimum precipitation of $Mg(OH)_2$.

EXPERIMENTAL

Apparatus

In Fig. 2 the scheme for the automatic determination of magnesium and calcium is shown; *a* is a sampler for a hundred samples with variable operational programme, and *b* is an 8-channel precision peristaltic pump, both constructed in our laboratory; *c* is a non-scanning double-beam spectrophotometer adapted for two micro-cells ("Photocrom" built by Rastelli, Rome). The stability, the wavelength-setting precision and the half-intensity bandwidth (less than 1 nm at 571 nm for a slitwidth of 0·2 mm) of this low-cost instrument were satisfactory for the present purpose.

The sampler was programmed for 30 analyses per hr. After each sample (0·15 ± 0·009 ml) a 0·75-ml portion of pure water was pumped through the same channel in order to clean the tubing system. The scheme does not provide for the use of air bubbles for liquid segmentation and tube cleaning. It was found that the accuracy and precision were not improved by air-bubbling, and that with the system used a higher or lower concentration of determinant in the preceding sample had no effect on the value determined.

Solutions

All solutions except the sample were buffered at pH 10 with a borate buffer. The concentration of buffer in the solutions was adjusted to be about 0·1*M*. A variation in buffer concentration between

0·05 and 0·2*M* did not affect the results. The concentration of EBT was about 0·01%. Since the final concentration of EBT was the same in both sample and reference cells, equation (1*a*) was used for the calculation of concentration. The concentrations of the other reagents are given in Fig. 2.

The operating steps were: (1) pumping of reagents 1, 3, 4, 5 and determination of magnesium for all the samples, according to equation (1*a*) and a calibration curve; (2) pumping of reagents 1, 2, 4, 5 and determination of calcium from the difference in absorbance between steps 2 and 1.

RESULTS AND DISCUSSION

From the calibration curve, a slope of 0·014 absorbance units per 1 ppm of metal was found; the lowness of this value has mainly to be attributed to the fact that the magnesium concentrations are referred to the original concentration in the sample, while the concentration in the optical cell is only about 7% of this, in order to have an excess of EBT even when 40 ppm of calcium and/or magnesium are present in the sample.

Two criticisms may therefore be raised concerning sources of error; the low absorbance values and the effect of incorrect repositioning of the monochromator at the isosbestic point. As to the first point, improvements in electronics have enabled instruments to be constructed with very good stability of amplifiers and light intensities. Secondly, an error of 0·5 nm in wavelength was found to have very little effect on the results, since variation of the ratio of the molar absorptivities of calcium-EBT complex and free EBT with wavelength is small near 571 nm. For instance, with a solution containing 40 ppm of calcium and 3 ppm of magnesium, a 0·5-nm wavelength-setting error was calculated to cause an error of 10% or less in the magnesium result, depending on the bandwidth.

Table I reports the analyses of some relevant samples and shows that the relative standard deviation is about 4% (10 measurements for each set).

TABLE I.—ANALYSIS OF CALCIUM–MAGNESIUM MIXTURES

No.	Sample composition, *ppm*		*Ca found, *ppm*	Relative std. devn. for Ca, %	*Mg found, *ppm*	Relative std. devn. for Mg, %
	Ca	Mg				
1	10	3	9·5	5·0	3·1	3·0
2	40	3	40·9	5·0	3·2	7·0
3	30	5	30·5 (29·6)	3·2 (3·4)	4·8 (4·8)	3·1 (3·8)
4	15	15	14·5 (15·3)	3·7 (1·0)	15·7 (16·1)	1·7 (1·5)
5	5	25	4·5 (4·6)	3·8 (5·1)	24·2 (25·2)	2·2 (1·6)

* Average value from ten determinations.

The numbers in brackets refer to experiments with liquid segmentation.

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Summary—Magnesium and calcium may each be determined in water by an automatic spectrophotometric method. At 571 nm with an excess of Eriochrome Black T as metallochromic agent, the variation in absorbance is proportional to the magnesium concentration regardless of the calcium concentration. By addition of MgEDTA to displace the calcium from its CaEBT complex, this element may be determined at the same wavelength. For 3–25 ppm of magnesium and 5–40 ppm calcium, the standard deviation was about 4%. The apparatus is described.

Zusammenfassung—Magnesium und Calcium können beide in Wasser mit einer automatischen spektrophotometrischen Methode bestimmt werden. Die Extinktionsänderung bei 571 nm mit einem Überschuß Eriochromschwarz T als Metallfarbreagens ist proportional zur Magnesiumkonzentration, unabhängig von der Calcium-konzentration. Fügt man MgEDTA zu, um das Calcium aus seinem Komplex mit Eriochromschwarz T freizusetzen, so kann Calcium bei derselben Wellenlänge bestimmt werden. Bei 3–25 ppm Magnesium und 5–40 ppm Calcium betrug die Standardabweichung etwa 4%. Die Apparatur wird beschrieben.

Résumé—On peut doser le magnésium et le calcium dans l'eau par une méthode spectrophotométrique automatique. A 571 nm avec un excès de Noir Eriochrome T comme agent métallochrome, la variation de l'absorption est proportionnelle à la concentration en magnésium, sans tenir compte de la concentration en calcium. Par addition de Mg EDTA pour déplacer le calcium de son complexe Ca EBT, on peut déterminer cet élément à la même longueur d'onde. Pour 3–25 p.p.m. de magnésium et 5–40 p.p.m. de calcium, l'écart type est d'environ 4%. On décrit l'appareil.

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Analysis of platinum for certain elemental impurities by neutron activation

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THE PRESENCE of certain elemental impurities in platinum, even in trace concentrations, may seriously limit its catalytic characteristics. Several radiochemical procedures are currently reported for assay of Fe, Co, As, Se, Ru, Pd, Ag, Os, Ir and Au in platinum.[1–6] In the present work, platinum is simultaneously analysed for Ag, Ru, Co, Fe, Zn, Cd and Hg by a scheme based on their sequential separation by ion-exchange chromatography.

EXPERIMENTAL

Materials and pile irradiations

The matrix target was processed from analytical grade platinum chloride ($H_2PtCl_6 \cdot 6H_2O$), by reduction with formic acid at pH 1·5. A second platinum sample was a 0·5-mm diameter platinum wire of analytical standard grade. The monitoring standards were spectroscopically pure, and all other chemicals were of analytical grade purity. The ruthenium standard was prepared by the reduction of a ruthenium trichloride solution.

The ion-exchange resin used was the strongly basic Dowex-1 (X8, 100–200 mesh), freed from alcohol-soluble organic compounds, and successively washed with water and concentrated hydrochloric acid.

The neutron activation was carried out in UA-RR-1 at Inchas for 48 hr with a neutron flux of $1{\cdot}3 \times 10^{11}$ n/mm²/sec. Test samples and standards were wrapped separately in aluminium foil (>99·95% pure) and subjected to the same neutron dose.

Radiochemical procedure

After a suitable cooling period, each sample is dissolved in 5–10 ml of *aqua regia*, then the solution is evaporated to dryness and the residue dissolved in concentrated nitric acid (5 ml). Aliquots of standardized carrier solutions of Ag, Ru, Co, Fe, Zn, Cd and Hg (50 mg each) are added. The separation and decontamination of the elements takes place simultaneously.

Silver. The nitric acid solution of test sample and added carriers is treated with 10 ml of hydrochloric acid (1 + 1), boiled, and the silver chloride precipitated is dissolved in excess of ammonia. Iron scavenger (5 mg) is added, and the iron(III) hydroxide is precipitated by addition of ammonia before further precipitation of silver as chloride.