

ION-EXCHANGE FLAME PHOTOMETRIC DETERMINATION OF SODIUM, POTASSIUM, CALCIUM AND MAGNESIUM IN THE ASH OF TOBACCO AND OTHER PLANTS

R.A. SHAH, A.A. QADRI AND NASIM AKHTAR BHATTI

Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

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Na, K, Ca and Mg in the presence of anions like phosphate and sulphate are estimated here in plant ash using Unicam Sp 900 flame spectro photometer. The interference of the anions and cations with each other has been overcome by using cation-exchange resin. The results are compared with those obtained by conventional procedures.

Introduction

The flame photometer is of particular advantage for the analysis of plant ash since it allows multiple determinations of sodium, potassium, calcium and magnesium in the presence of phosphate and sulphate ions. The classical methods are time-consuming and difficult for an average analytical worker to perform accurately. The radiant energy emissions of the metal ions are affected by the presence of other ions. The error produced may be positive or negative and the amount of the error is dependent upon the concentration and identity of the metal involved. A number of references are found in literature where attempts have been made to determine these elements in the presence of one another.

The presence of potassium decreases the emission of sodium. The effect becomes relatively less as the sodium concentration increases with respect to potassium.¹ The determination of calcium is subject to interference by the presence of magnesium and phosphate. Mosher, Bird and Boyle² have reported the depression of calcium emission by larger concentration of magnesium. Calcium of course is separated by precipitation with oxalate.³ West, Folse and Montgomery⁴ have obviated the interfering effect of the diverse ions by the radiation buffers. Parks et al.⁵ have shown that phosphate had a pronounced inhibiting effect on the flame intensity of potassium but less effect on sodium. Dipple Bricker and Furman⁶ state that the emission intensity of calcium varies linearly and inversely with phosphate concentration. Sugawara, Koyama and Kawasaki⁷ separated magnesium from calcium and strontium by precipitating the oxalates of calcium and strontium in the presence of urea. Cooley⁸ buffers the phosphate effect by adding an excess of phosphate ion so as to give a limiting depression. Takahashi and Yoshida⁹ have compensated the depressive effect of the phosphate ions on the calcium emission by using potassium and also sulphuric acid as radiation buffers. Grewelling¹⁰ determined calcium and magnesium in plant materials by the

resolution of anion interference by using ethylene diamine tetraacetic acid salts. This integrated procedure works well with potassium, calcium and magnesium, but, in the presence of sodium, calcium has to be removed by precipitation because it causes a positive error. Attempts were also made to remove the phosphate interference by the addition of zirconium nitrate;¹¹ this however also reduces the calcium emission, as do the phosphates.

In the present work, the interference due to anions like phosphate and sulphate was removed by passing the solution of the ash after the removal of silica through a column of cation exchange resin in the hydrogen form. The phosphate and sulphate ions pass through, while the cations are retained by the column. The interference of the cation with one another has been overcome by elution of the cations from the exchange column selectively with varying strengths of hydrochloric acid. The effect of calcium and magnesium on each other and the effect of sodium on calcium has in this way been completely eliminated, thus making the estimations easier and more accurate than the conventional procedure adopted for flame photometric estimations.

Experimental

In order to establish the conditions for the elution of these cations, known solutions, of Na, K, Ca and Mg were first passed individually through the ion-exchange column and different strengths of HCl were used to eluate these cations separately. The eluates were collected in fractions of 10 ml. each and the eluates tested for the cation being eluated. In this manner the strength and volume of HCl required to eluate a particular ion was established for the length of the column mentioned. However, if the change in the length of column is necessitated by the higher concentration of a particular ion, new eluation condition can be easily established. A solution containing a mixture of Na, K, Ca and Mg was then passed through the column. Sodium and calcium were eluated

separately with 0.5N and 2N HCl while potassium and magnesium have been eluted together with 1N HCl (Fig. 1). Since potassium does not effect the emission of Mg and magnesium does not interfere with potassium emission as shown in Fig. 2, there was no need to make any attempt to eluate them separately.

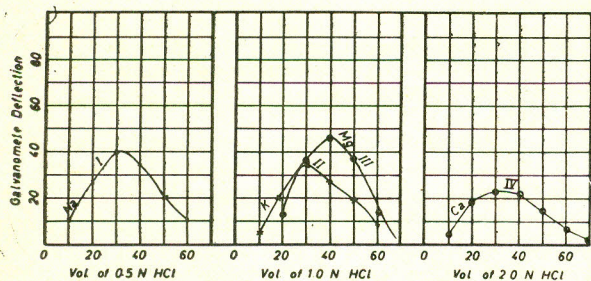


Fig. 1.—Elution of Na, K, Ca and Mg cations from the mixture.

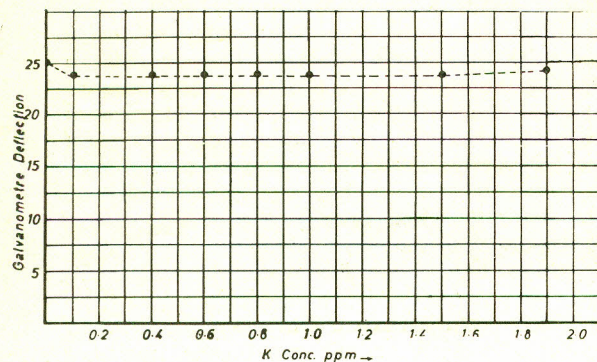


Fig. 2 (a).—Effect of increasing K. Conc., on a transmission of 2 p.p.m. Mg. Sol. $\lambda_c = 2852 \text{ \AA}$.

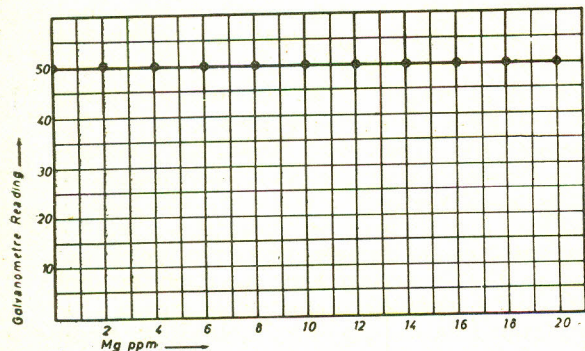


Fig. 2 (b).—Effect of varying magnesium concentration on K emission.

Effect of Iron.—Iron in the range of 100 p.p.m. has no effect on the emission of calcium and magnesium.¹²

Effect of Acid Content.—As the eluation of the cations is being effected by using different normalities of hydrochloric acid, some change in emission is to be expected because the increased acidity depresses emission.¹³ The extent to which the emission is depressed with 0.5N, 1N and 2N HCl is shown in Figs. 3 and 4. This effect was corrected by setting the galvanometer zero using 0.5N

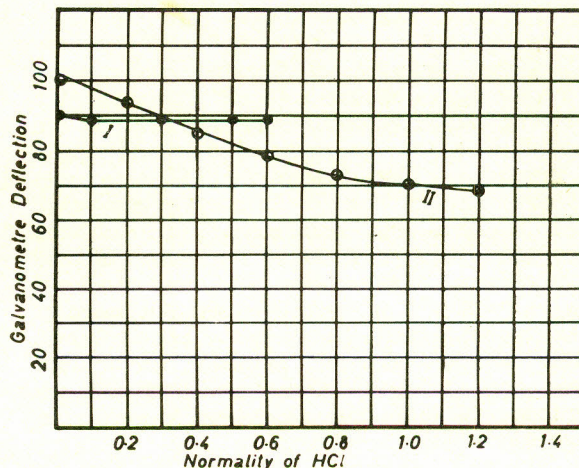


Fig. 3.—(I) Effect of HCl on Na emission (II) Effect of HCl on K emission.

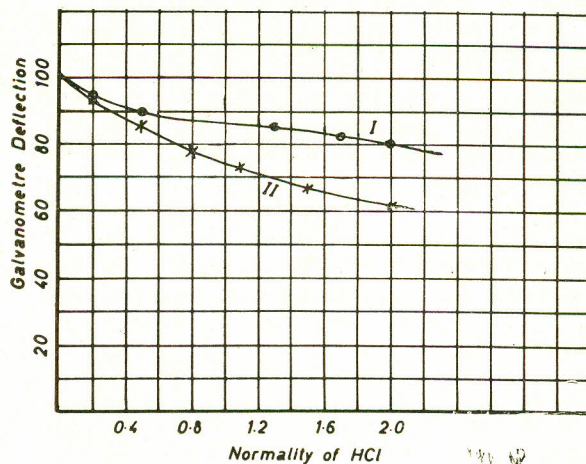


Fig. 4.—(I) Effect of increase acid (HCl) content on Ca transmission; 10 p.p.m. Ca Sol. set to 100 $\lambda_c = 4227 \text{ \AA}$ (II) Effect of increasing acid content on 25 p.p.m. Mg. Sol. $\lambda_c = 2852 \text{ \AA}$

HCl, 1N HCl and 2N HCl concentration in the case of Na, K and Mg and Ca, respectively.

Apparatus

1. Flame spectrophotometer (Unicam) SP 900
2. Quickfit glass columns No. CR12/10
14.2 cm. length 1.25 cm. (Ext.) diameter.

Reagents

1. Cation Exchange resin Amberlite. IR (120)H
2. Deionized water.
3. Hydrochloric acid A.R.
4. Sodium chloride A.R.
5. Calcium carbonate A.R.
6. Magnesium sulphate 7H₂O A.R.

Procedure

15—20 mg. of the plant ash are dissolved in hydrochloric acid, and silica is removed by the usual method. The solution, obtained after filtering off silica, is passed through a column of Amberlite IR (120)H ion-exchange resin (length 10 cm.) at a flow rate of 3 ml./min. The column is then washed with 50—60 ml. of deionized water to remove the phosphate and sulphate ions completely.

(i) *Sodium Determination.*—The column is then treated with 60 ml. of 0.5 N HCl to eluate the sodium ion. The washings are then made up to 100 ml. in a graduated flask with 0.5 N HCl and sodium determined in this solution (a) as follows:

The sensitivity of SP 900 at wave length 5890A° is adjusted to give a galvanometer deflection of 100 with 10 p.p.m. of Na. The instrument is initially set to zero with 0.5 N HCl. The galvanometer reading with the solution (a) is noted; if the reading exceeds full scale, then further dilute the solution and read the concentration of sodium corresponding to the galvanometer reading from the calibration curve of Na.

$$\% \text{ of Na}_2\text{O} = \frac{\text{ppm of sodium} \times 10 \times 1.348}{\text{wt. of ash in mg.}}$$

(ii) *Potassium and Magnesium Determination.*—The ion-exchange column is further washed with 75 ml. of 1N HCl and the volume made to 100 ml. with 1N HCl. Potassium and magnesium are determined from this solution (b). The galvanometer is adjusted at wavelength 7665 A° to give a deflection 100 with potassium solution of 10 ppm. Read the concentration of potassium from

the calibration curve of potassium corresponding to the galvanometer reading and calculate the % of potassium oxide.

$$\% \text{ K}_2\text{O} = \frac{10 \times \text{ppm of potassium} \times 1.205}{\text{wt. of ash in mg.}}$$

(iii) *Magnesium Determination.*—The solution (b) used for potassium determination is also used for the estimation of magnesium. The galvanometer of SP 900 is set at 2852 A° and the concentration of Mg corresponding to the galvanometer deflection is read from the calibration curve and % of magnesium oxide calculated.

$$\% \text{ MgO} = \frac{10 \times \text{ppm} \times 1.658}{\text{wt. of ash in mg.}}$$

(iv) *Calcium Determination.*—The column is next eluated with 75 ml. of 2N HCl and the volume made to 100 ml. with 2N HCl and then diluted to 200 ml. with deionized water so that the resulting solution (c) has a normality of 1N HCl. This dilution was made in order to lessen the attack of the solution on the burner. The instrument was set at 4226 A°, and the deflection due to solution (c) was measured. The concentration of calcium was read from the calibration curve and the % of calcium oxide determined.

$$\% \text{ CaO} = \frac{10 \times \text{ppm} \times 2 \times 1.399}{\text{wt. of ash in mg.}}$$

Calibration Curves

The calibration curves for sodium, potassium, calcium and magnesium are obtained on solutions prepared as below.

Sodium.—A stock solution of sodium was prepared by dissolving 0.2542 g. of sodium chloride A.R. per litre (Na 100 ppm) 19 ml. of this solution are diluted to 100 ml. after the addition of 25 ml. of 2 N HCl. This solution contains 10 ppm of sodium in 0.5 N HCl. From this solution, standards containing 2, 4, 6, 8, ppm of sodium in 0.5 N HCl are prepared.

Potassium (100 ppm).—Dissolve 0.1907 g. of KCl (A.R.) in one litre. 10 ml. of this stock solution and 50 ml. of 2 N HCl are diluted to 100 ml. This will correspond to 10 ppm of K in 1N HCl. From this solution, standards containing 2, 4, 6, 8, ppm of potassium in 1 N HCl are prepared.

Magnesium (1000 ppm).—Dissolve 10.136 g. of Mg So₄ 7H₂O A.R. in 1 litre. 100 ml. of this

solution when diluted to one litre will give a solution containing 100 ppm of Mg 25 ml. of this solution and 50 ml. of 2N HCl are diluted to 100 ml. to yield a solution containing 25 ppm of Mg in 1N HCl. Standards containing 5, 10, 15, 20, 25, ppm of Mg in 1N HCl were prepared.

ciated with determining the various cations in the presence of phosphate ions have been eliminated by simply using selective eluation and then estimating these cations individually by the flame spectrophotometer. Many errors and difficulties which may be caused by using external agents for

TABLE I.

S. No.	Tobacco grade No.	% CaO		% MgO		% Na ₂ O	% K ₂ O
		SP 900	Classical	SP 900	Classical	SP 900	SP 900
1	FC/A	32.45	32.87	11.81	12.12	0.92	3.16
2	BFS	27.52	27.81	8.02	8.12	1.52	2.86
3	BV	30.98	31.10	7.65	7.48	0.98	3.1
4	SS/TGD	27.51	27.33	8.29	8.04	1.31	2.32
5	Dust dryer	18.29	18.17	5.13	4.86	2.1	5.4
6	EBE	20.30	20.20	11.51	11.71	0.85	8.51
7	CIG	10.5	10.20	8.3	8.51	0.48	1.90

Calcium (100 ppm).—0.2498 g. of calcium carbonate A.R. dissolved in minimum amount of hydrochloric acid, evaporated, and then dissolved in 1000 ml. of deionized water. 10 ml. of this solution and 50 ml. of 2N HCl are diluted to 100 ml. (1 ppm of Ca). Standards containing 2, 4, 6, 8, ppm of calcium are prepared.

The main settings of the instrument used are as follows:

Sodium line	5890 A°	Air pressure 28 P.S.I.	
Potassium line	7665 A°	Gas pressure 12.6 mm. (acetylene)	
Calcium line	4227 A°		
Magnesium line	2852 A°	Slit	0.08 mm.
Shutter filter for sodium	.. position		4
.. .. potassium		3
.. .. magnesium		2
.. .. calcium		3

All the curves are straight lines.

Six samples of the ash were analysed by classical method and also using the method described in this text. The results are shown in Table I.

Discussion

The method described has the advantage of being straightforward, less time consuming and easy to perform. Many of the difficulties usually asso-

ciated with determining the various cations in the presence of phosphate ions are also avoided. Very small amount of ash samples can therefore be handled successfully in this manner.

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