

# THE APPLICATION OF EMISSION SPECTROGRAPHY TO PHARMACEUTICAL ANALYSIS

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Received July 2, 1952

ALTHOUGH spectrographic methods of analysis are initially expensive when compared with the more classical methods because of the high cost of much of the equipment used, nevertheless such methods, particularly those involving emission spectrography are becoming increasingly popular. This is because in some cases the work cannot be done by purely chemical means, while at other times emission spectrography may prove more accurate, and certainly in the majority of instances there is a considerable saving of time. The last point is of paramount importance, particularly in large laboratories concerned with the control of manufacturing processes. Another reason for favouring such methods is the small amount of sample needed and the fact that even on this small amount the presence of a considerable number of elements can be determined qualitatively or quantitatively.

Emission spectrography has been in use for some time for the determination of traces but its application to pharmaceutical analysis, which demands also the estimation of major constituents, has not been widely reported, probably because it was not considered sufficiently accurate for this purpose. The introduction of new techniques, particularly those involving solution methods has enabled these difficulties to be overcome. One of the most tedious and certainly the most difficult feature of methods involving the spectrographic analysis of powders is the preparation of homogeneous standards and samples, but the use of solution methods obviates this difficulty. In this way solution methods have a great advantage over the older powder methods and the increased accuracy associated with them makes them ideally suitable for application to pharmaceutical analysis. In our laboratory two such methods are finding increasing application and our experience has shown that in both cases an accuracy within 2 per cent. can be obtained in routine assays. These two methods are those involving flame photometry and the porous-cup technique.

## FLAME PHOTOMETRY

The use of flame photometers of varying design for the simple determination of the alkalis has become fairly widespread. In planning and building the flame photometer in use in this laboratory a wider application was envisaged and already the range of elements examined by this method has been considerably extended. The instrument is one described by Brealey and Ross<sup>1</sup> and can be used with either an air-propane or an air-acetylene flame. The use of such an instrument for the estimation of sodium and potassium is well known and indeed it has proved so

successful in this laboratory that these two elements are not normally determined by any other method. The routine control of fertilisers is carried out by this method and Table I, taken from the paper by Brealey,<sup>2</sup> will serve to show the agreement between results obtained by the official<sup>3</sup> chemical method and by flame photometry.

TABLE I

Sample	Potassium oxide, K <sub>2</sub> O	
	Flame photometry per cent.	Chemical per cent.
G1	8.07	8.12
G2	7.66	7.73
G3	8.77	8.61
G4	10.00	10.27
G5	7.95	7.96
G6	8.20	8.20
T1	11.65	11.58
T2	10.40	10.29
T3	12.25	11.93
T4	10.40	10.53
T5	9.05	8.83
T6	9.88	9.74

The starting material for the manufacture of all potassium salts is either potassium carbonate or potassium hydroxide, which always contain some of the corresponding sodium compound. This contamination subsequently appears to a greater or less extent in the finished product, depending on the particular salt being manufactured. A great deal of interest has been shown recently in this problem, and flame photometry offers the ideal method of determining sodium in potassium salts.

The examination of a number of potassium salts (Table II) has revealed the fact that this contamination is often considerable and there is no doubt that the future will see ever-increasing use of this method for such determinations because of the small amount of time and labour needed in carrying them out once the method has been established. In the past such estimations have been somewhat neglected, for want of a quick, reliable method.

TABLE II

Potassium salt	Corresponding sodium salt per cent.
Citrate	2.4, 5.1, 7.6, 8.8
Acetate	5.4, 5.7
Iodide	0.31, 0.22, 0.42, 0.34
Chloride	0.72
Bromide	0.14, 1.2, 0.54, 1.0
Sulphate	7.1, 5.6, 3.1, 3.5
Chlorate	0.02
Bicarbonate	0.15
Acid tartrate	0.49
Carbonate	3.0, 4.5, 1.0, 1.9
Hydroxide	1.0, 0.91

problem to find means of extracting any required element from an insoluble material.

Before the estimation of a particular element can become a routine process a certain amount of investigational work has to be carried out on the photometric side of the method in order to determine the sensitivity range of the element and also the extent of interference from extraneous elements. The following determinations of lithium may be cited as examples of how such problems are approached.

The first was a determination of lithium and was required for its estimation in "kidney pills" which contain 6 per cent. of lithium benzoate in a vegetable extract base. As no simple specific chemical method was

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available the problem was submitted for investigation by flame photometry.

Since the vegetable extract contains sodium and potassium salts it was decided to use the air-propane flame because it is known that this flame exhibits less interference from cations than the hotter air-acetylene flame. Standard solutions of 1000, 100 and 10 p.p.m. of lithium in water were prepared and examined. It was found that a full scale deflection of the galvanometer could be obtained with the 10 p.p.m. standard using the 6707 Å line. Further standards of 2, 4, 6, 8 p.p.m. of lithium were then prepared and the readings obtained showed that lithium gives a linear response over the range 0 to 10 p.p.m.

The effect of the sodium, potassium and benzoate ions was then studied and it was shown that the benzoate ion in large excess of the amount actually combined with the lithium in the pills has no effect on the lithium standards. Similarly potassium has no effect but sodium causes a strong enhancement as shown by Table III.

TABLE III

Li (p.p.m.)	Interfering ion	Concentration of interfering ion (p.p.m.)	Error per cent.
2	Na <sup>+</sup>	10	+40
2	"	100	+70
2	"	1000	+125
5	"	10	+6
5	"	100	+22
5	"	1000	+58
8	"	10	+1
8	"	100	+14
8	"	1000	>25

Having noted the serious errors caused by the presence of sodium, the actual amount present in the final solution to be used was determined and found to be only 2 p.p.m. It can be seen from Table III that the effect of this amount of sodium on 6 to 7 p.p.m. of lithium is negligible. The following method for the determination of the lithium content of the pills was then adopted: 20 pills were ground and 1 g. of the mixture heated with 100 ml. of water on a steam bath for 20 minutes. The solution was cooled, diluted to 500 ml. and filtered. The filtrate was examined on the flame photometer.

In the above example it can be seen that although interfering elements were present, the amounts were not sufficient to cause inaccuracies in the lithium estimation. These suitable conditions are not however always present and other methods have to be adopted to overcome interference effects.

An example of this is the estimation of lithium in effervescent granules of lithium citrate. These contain about 0.3 per cent. of lithium together with about 40 times as much sodium, and the possibility of determining the lithium content by flame photometry was investigated. It was already known from the work carried out on the "kidney pills" that over the range 0 to 10 p.p.m. lithium gives a linear response and that sodium has a considerable enhancement effect, which we think is due to the background

caused by the close proximity of the sodium doublet at 5890/6 Å to lithium at 6707 Å. Since the sodium could not be removed chemically the possibility of correcting in some way for its effect was examined.

The first method investigated, although abortive, is instructive as an illustration of the approach that is made to the solution of such problems. It was thought that a reading taken at the lithium wavelength (6707 Å) would represent the lithium plus sodium and that a reading taken at some nearby wavelength would represent the sodium alone, so that the difference between these two readings would give a measure of the lithium.

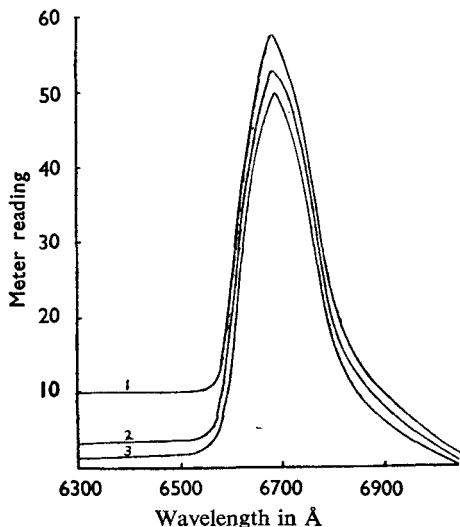


FIG. 1.

1. 5 p.p.m. of lithium + 300 p.p.m. of sodium.
2. 5 p.p.m. of lithium + 50 p.p.m. of sodium.
3. 5 p.p.m. of lithium.

This method gives an overcorrection as the difference in all cases should be equivalent to 5 p.p.m. of lithium (i.e., a galvanometer reading of 50). This overcorrection is probably due to the fact that there is another lithium line at 6104 Å which causes a small reading at 6500 Å so that the reading at this latter wavelength is not due to the sodium alone. This method was considered unsatisfactory.

TABLE IV

Li p.p.m.	+ Na p.p.m.	(A) Reading	Na p.p.m.	(B) Reading	(A)-(B)	Theoretical reading
3	100	41.0	100	10.5	30.5	30
3	500	52.0	500	22.0	30.0	30
3	1000	64.0	1000	34.0	30.0	30
5	100	60.5	100	10.5	50.0	50
5	500	72.0	500	22.0	50.0	50
5	1000	85.0	1000	34.0	51.0	50
7	100	81.0	100	10.5	70.5	70
7	500	91.0	500	22.0	69.0	70
7	1000	96.0	1000	34.0	62.0	70

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In the next method investigated a reading was obtained at 6707 Å, (due to lithium plus sodium), and at the same wavelength a reading was obtained for the sodium alone. Since the reading for the sodium was comparatively low at this wavelength the difference was taken as a measure of the lithium present. The results obtained are shown in Table IV and it can be seen that except for one bad result at 7 p.p.m. of lithium plus 1000 p.p.m. of sodium the results obtained are very close to those expected on theoretical grounds.

This method was then applied to a batch of granules.

### Experiment 1

10 g. was dissolved in water and diluted to 1 l. and 10 ml. of this was diluted to 100 ml. (solution A). A further dilution of 10 to 100 ml. of solution A was made to give solution B. The sodium content of solution B was estimated in the normal way on the flame photometer and found to be 14.6 p.p.m. Solution C, containing 146 p.p.m. of sodium, was then prepared. Solutions A and C were then read at 6707 Å and gave the following results: solution A, 50; solution C, 13; difference, 37  $\equiv$  3.7 p.p.m. of lithium. This is equivalent to a lithium citrate content of 5.0 per cent.

for the granules. This result is rather higher than expected (theoretical content is 4.5 per cent.) but the accuracy of the method was eventually proved as follows.

### Experiment 2

Solution A (as in experiment 1) was made stronger by taking a dilution of 15 to 100 ml. of the original granule solution and solution C was 220 p.p.m. of sodium. These were read as in experiment 1 and gave the following results: solution A, 69; solution C, 14; difference 55  $\equiv$  5.5 p.p.m. of lithium. This is again equivalent to 5.0 per cent. of lithium citrate in the granules.

### Experiment 3

This involved a recovery experiment and was carried out by using solution A as in experiment 1 to which the equivalent of 2.0 p.p.m. of lithium was added. Solution C was the same as in experiment 1 and the following results were obtained: solution A + 2 p.p.m. of lithium, 70;

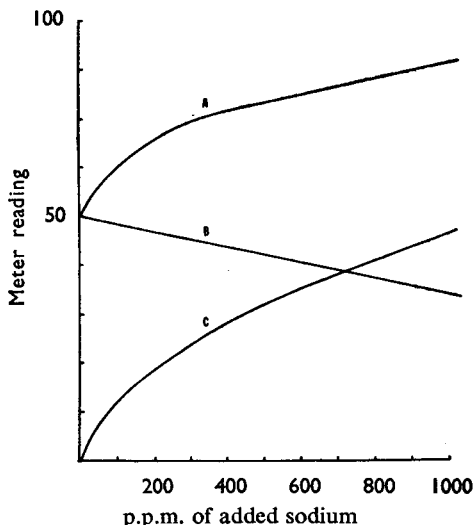


FIG. 2. A. 5 p.p.m. of lithium 6707Å.  
B. Difference.  
C. 5 p.p.m. of lithium 6500Å.

solution C, 13; difference  $57 \equiv 5.7$  p.p.m. of lithium. The difference between this and solution A (3.7 p.p.m. of lithium) is 2.0 p.p.m. of lithium which is equivalent to a 100 per cent. recovery. From the results obtained there seems no doubt that this method of compensating for the interference effect of sodium on lithium provides a reliable means of estimating lithium in such granules.

TABLE V

Concentration of Ca (p.p.m.)	Normality of $\text{PO}_4$	Error per cent.
50	0.1	-61
50	0.01	-56
50	0.001	-13
5	0.1	-7
5	0.01	-5
5	0.001	-3

The estimation of calcium in the presence of phosphate provides a further means of overcoming the effect of an interfering ion. In this instance the interfering ion depresses the readings due to calcium as shown in Table V. Experiment showed that if increasing amounts of phosphate in the form of ammonium phosphate were added to a fixed amount of calcium a concentration of phosphate was eventually reached beyond which there was no further alteration of the calcium reading. This is illustrated in Table VI.

TABLE VI

Concentration of Ca (p.p.m.)	Concentration of $\text{PO}_4$ (mg./ml.)	Ca found (p.p.m.)
5	0.005	4.85
5	0.01	4.45
5	0.05	4.25
5	0.1	4.3
5	0.5	4.4
5	1.0	4.4
5	1.5	4.4
5	2.0	4.4

Similar results are obtained with solutions containing 50 p.p.m. of calcium and concentrations of phosphate in excess of 0.5 mg./ml. Since no sample examined contains such a high proportion of phosphate in relation to the calcium content, this concentration of phosphate is always added to the solutions of standards and samples prepared for flame photometry. This added phosphate being of very high concentration compared with that present in the sample, eliminates errors due to variations in the amount contained in the sample.

The estimation of the potash content of fertilisers and of the contamination of sodium and potassium salts has been referred to above. Besides these routine applications, flame photometry is used in this laboratory for the estimation of potassium in such preparations as compound syrup of hypophosphites, compound syrup of glycerophosphates and various non-official galenicals. The work has also been extended to the determination of iron and manganese in various preparations. Iron is one of the less sensitive elements when excited in the flame and thus the range of standards used for its determination is 0 to 200 p.p.m. at wavelength 3736 Å with the acetylene flame. Sodium, potassium and calcium all interfere strongly with iron in quantities greater than 100 p.p.m. in the solution being examined and thus the application of flame photometry in this respect is, at the moment, somewhat limited until more work can be carried out with a view to eliminating these effects. Manganese gives a linear response over the range 0 to 100 p.p.m. with

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an acetylene flame at 4031 Å and has been estimated in ferrous sulphate after removal of the iron with results which agreed well with those obtained by chemical methods.

Many of the above estimations require nothing more than simple dilutions of the sample before submitting it to flame photometry. Other determinations require more complex manipulation, e.g., for copper in veterinary emulsions it was necessary to extract the sulphated ash 3 times with aqua regia, evaporate the extract to dryness and leach out the soluble copper salt with hot water. The range of standards used was 0 to 200 p.p.m. of copper at 3274 Å with the acetylene flame. The copper content of various bronzing powders has also been determined.

The great advantage of flame photometry lies in its application to routine analyses. However, from time to time, various problems arise which are not a routine matter but which can be most easily resolved by the use of flame photometry. In this laboratory, for instance, the calcium content of chicken bones has been examined as part of a large programme of investigational work and the sodium and potassium contents of various agars have been compared. Contamination problems of widely diverse natures have been investigated.

There can be no doubt of the superiority in many respects of flame photometry over other methods of analysis. The time-saving factor alone makes it worthy of serious consideration. Once solutions have been prepared the results on half-a-dozen samples can be reported within 15 minutes, which compares very favourably with the time taken, for instance, to estimate sodium, potassium and lithium in the presence of each other. In our opinion the latter estimations need the attention of skilled analysts, whereas flame photometric assays can be carried out by junior staff with comparatively little experience or skill. As far as accuracy is concerned flame photometry is at least as reliable as many other methods.

## THE POROUS-CUP TECHNIQUE

Many pharmaceutical powder preparations contain magnesium and silicon, often in the form of magnesium trisilicate and the estimation of these elements by chemical methods is a laborious process. In this laboratory, which is dealing with the routine checking of a large number of process samples, delay was frequently encountered, so it was necessary to look for other means of analysis. The porous-cup technique due to Feldman<sup>4</sup> was investigated and it proved to be a reliable alternative to the chemical method. A modification of this method is now employed in this laboratory for the routine determination of magnesium and silicon in all powders containing magnesium trisilicate. If any technique is to be of use in such applications its accuracy must be high and in our opinion a standard deviation of 2 per cent. is the maximum permissible. It has been shown that the method is capable of this accuracy.

In essence the method consists of pipetting a small quantity of solution into a cup electrode in the form of a narrow graphite cylinder open at the top end and with a base of a standard uniform thickness. Before

use the base is made porous by heating, so that during the passage of a spark the solution in the electrode passes continuously through it into the discharge. The lower electrode consists of solid graphite with the end turned to an  $80^\circ$  cone with a slightly flattened tip. The cup electrodes are easily drilled on a lathe from graphite rods, 10 such electrodes being obtained from 1 rod. The thickness of the base is adjusted by means of a special gauge and checked with the aid of a micrometer. The actual base thickness is not critical and in practice limits of  $40/1000$  inch  $\pm 3/1000$  inch are used, but the base of each electrode must be of consistent thickness otherwise erroneous results are obtained. The lower electrodes are made from 3-inch lengths of graphite rod turned to the required angle with a simple cutter similar in principle to a pencil sharpener, the tip being flattened with a small file. These lower electrodes can be re-sharpened continually until they become too short for further use, but the cup electrodes can only be used once. The cup electrodes in use in this laboratory are somewhat larger than those used by Feldman and the dimensions are shown in Figure 3.

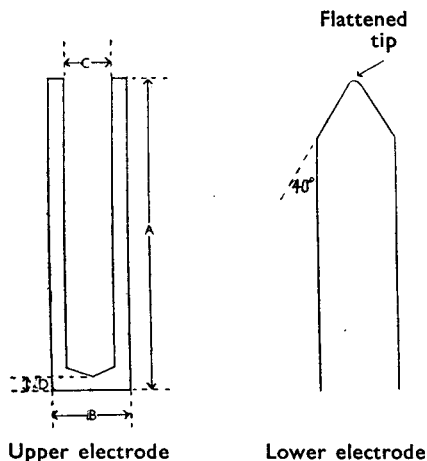


FIG. 3. A = 1 inch.  
B =  $1/4$  inch.  
C =  $5/32$  inch.  
D =  $40/1000$  inch.

During sparking, the solution from the upper cup electrode is fed continuously into the discharge. The estimation may be divided into three stages.

(a) *The preparation of solutions.*—Various methods were tried, including carbonate fusions, but the following technique was eventually evolved and proved to be the most satisfactory in the majority of cases where insoluble materials containing silica were involved.

A quantity of powder estimated to contain between 0.1 g. and 0.15 g. of  $\text{SiO}_2$  is accurately weighed into a platinum dish. 2 ml. of hydrochloric acid is added slowly and the mixture evaporated to dryness on a steam bath. 2.5 g. of potash pellets is added and warmed gently over a bunsen flame until liquid. After heating gently for a short time a clear solution results. The mass is allowed to cool and is then dissolved in 20 ml. of water. The resulting solution is acidified with 5 ml. of nitric acid, and transferred to a 50 ml. graduated flask containing 5 ml. of 0.5 per cent. sodium borate solution and 10 ml. of 1 per cent. potassium dichromate solution and diluted to volume. The boron acts as an internal standard for the estimation of the silicon and the chromium for the magnesium.

Standard solutions containing: (1) 0.015 per cent. of  $\text{SiO}_2$  + 0.025 per cent. of  $\text{MgO}$ ; (2) 0.025 per cent. of  $\text{SiO}_2$  + 0.035 per cent. of  $\text{MgO}$ ; (3) 0.035 per cent. of  $\text{SiO}_2$  + 0.045 per cent. of  $\text{MgO}$ ; and equivalent



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amounts of potassium hydroxide, nitric acid, sodium borate and potassium dichromate are prepared. If difficulty is encountered in obtaining clear solutions it has been found advantageous to use a 1:1 mixture of 60 per cent. perchloric acid and concentrated hydrochloric acid for the initial breakdown of the powder before the treatment with potash is carried out.

(b) *Recording of the Spectrograms.*—Before use, the base of each cup electrode is heated to a dull red heat in a blow lamp for 5 seconds in order to make it porous. These electrodes are mounted in the upper of 2 special stainless steel electrode holders attached to a de Gramont stand placed in such a position that the electrodes are 20.7 cm. from the entrance slit of a Hilger medium quartz spectrograph. An F1028 lens, focal length 16.5 cm., is positioned 2 cm. from the slit. The lower conical electrode is then positioned in the lower holder so that there is a gap of 2 mm. between the top of this electrode and the base of the cup electrode. 0.15 ml. of solution is pipetted into the cup electrode, care being taken to prevent the formation of air pockets which would cause the solution to bubble over when the spark is applied. In order to facilitate the filling of these electrodes the end of the pipette is drawn out into an elongated jet so that it reaches the bottom of the electrode cavity. 30 seconds are allowed to elapse for the solution to seep through the base of the electrode before a spark is applied for 40 seconds. The source unit used is the Hilger 15,000 v. condensed spark with 0.03 mH inductance. Ilford thin film half-tone plates are used to record the spectrograms and it is possible, using a slit height of 1 mm., to obtain 36 such spectra usually consisting of 3 standards and 9 samples each in triplicate on one plate. The plates are developed for 5 minutes in ID2 developer at 18.5° C., fixed for 10 minutes, washed for 20 minutes and allowed to dry.

(c) *Evaluation of the spectrograms.*—From the spectrograms the density differences of the line pairs Si 2516.1Å/B 2497.7Å and Mg 2790.9Å/Cr 2830.4Å are calculated from densitometer readings. Curves are plotted of these density differences against percentages of SiO<sub>2</sub> and MgO and from these the strengths of the unknown solutions are computed.

Silicon and magnesium were the first elements for which this technique was worked out in this laboratory. This involved finding the means of getting the powders into solution, investigating the sensitivity ranges of all the elements concerned, finding suitable internal standards and finally determining the accuracy of which the method was capable. It is of interest to note here that until boron was adopted as the internal standard for the silicon the method proved quite unsatisfactory. No difficulty has been encountered from the presence of boron in the electrodes. It was also proved that there is no interference between the magnesium and silicon; in other words the amount of either element present does not affect the accuracy of the determination of the other.

Table VII shows the results obtained on a sample of powder containing magnesium trisilicate, magnesium carbonate and sodium bicarbonate

which was examined for the purpose of obtaining an estimate of the accuracy of the method:

TABLE VII

SiO <sub>2</sub> per cent.			
18.7	19.5	19.3	Plate 1
18.6	17.8	17.9	" 2
17.7	17.6	18.5	" 3
18.1	18.6	18.7	" 4
18.5	18.4	19.0	" 5
Average 18.5 per cent.			
These results show a standard deviation of 3.3 per cent. for individual determinations which is reduced to 1.9 per cent. when the sample is examined in triplicate.			
MgO per cent.			
24.7	23.8	24.7	Plate 1
23.1	23.6	23.8	" 2
22.9	22.9	22.8	" 3
23.8	22.0	23.1	" 4
22.1	22.8	21.5	" 5
Average 23.2 per cent.			
The results show a standard deviation of 3.5 per cent. for individual determinations, 2.0 per cent. for triplicate determinations.			

For comparison purposes Table VIII gives the results obtained spectrographically and chemically on 5 samples of compound powder of magnesium trisilicate.

TABLE VIII

Batch number	SiO <sub>2</sub>	
	Chemically per cent.	Spectrographically per cent.
5006 H	13.3	13.7
5007 H	12.8	13.3
5008 H	13.6	14.2
5009 H	13.3	13.2
5011 H	13.8	13.9

It can be seen that this method provides a reliable alternative to chemical methods of assay. In practice 10 samples per day can be examined in triplicate for both the silicon and magnesium content by one person, showing a great saving in time over other methods. Once the technique had been thoroughly investigated and methods worked out, it became an easy matter to adapt it to the determination of other elements. For instance, the method has been used to determine the amount of aluminium and magnesium present in samples containing 1 per cent. of MgO and 3.5 per cent. of Al<sub>2</sub>O<sub>3</sub>. The solution of the samples presented no difficulty when the method already outlined for magnesium trisilicate powders was adopted. Aluminium was found to be extremely sensitive and the following composite standards were employed: (1) 0.015 per cent. of MgO + 0.004 per cent. of Al<sub>2</sub>O<sub>3</sub>; (2) 0.020 per cent. of MgO + 0.008 per cent. of Al<sub>2</sub>O<sub>3</sub>; (3) 0.025 per cent. of MgO + 0.012 per cent. of Al<sub>2</sub>O<sub>3</sub>; each with the addition of 0.1 per cent. of potassium dichromate.

Chromium was used in this case as internal standard for both the magnesium and aluminium.

This method also gives a considerable saving in time over the chemical assay and it is possible for one person to carry out the examination in about 3½ hours. It would be possible for about a dozen samples to be examined in 6 hours. One particular sample was examined both chemically and spectrographically and gave the following results: MgO

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per cent.—chemically, 1.06, spectrographically, 1.11;  $\text{Al}_2\text{O}_3$  per cent.—chemically, 3.44, spectrographically, 3.36.

The uses of the porous-cup technique already described prove it to be a speedy and accurate method for the determination of major constituents. The method can also be used for the determination of traces. An example of this is the estimation of zinc in iron salts. These estimations were formerly carried out polarographically but the great advantage of a spectrographic determination is that the presence of zinc can be positively identified by the presence of a trio of lines at  $3282.3\text{\AA}$ ,  $3302.0\text{\AA}$  and  $3345.0\text{\AA}$  even in the presence of a small amount of iron whereas the polarographic method is not necessarily specific in the possible presence of other impurities. Zinc standards in the range 100 to 1000 p.p.m. are employed and as the method permits the concentration or dilution of the sample a considerable range of zinc content can be determined. This range has been found the most suitable for the majority of samples, but by sparking 0.25 ml. of solution for 2 minutes the range 20 to 200 p.p.m. has also been used. Once again the method has proved to be sufficiently speedy to permit the investigation by one person of up to 10 samples in triplicate in one day.

Because of the complex iron spectrum the main problem in the application of the method is the removal of the greater part of the iron and this is accomplished as follows. A suitable amount of the sample (usually 5 g. for solids and 10 ml. for solutions) is dissolved in 10 ml. of hydrochloric acid and warmed on the steam bath. Sufficient nitric acid is then added to ensure complete oxidation of the solution which is then cooled, transferred to a separator and extracted with 50 ml. of ether. After separation of the aqueous phase a further 10 ml. of hydrochloric acid is added and the solution again extracted with 50 ml. of ether. Further extractions are carried out, if necessary, in the same way until the aqueous phase is colourless, after which it is evaporated to dryness. The residue is dissolved in a suitable quantity of 0.25 per cent. cadmium sulphate solution (usually 5 ml.) and centrifuged if necessary to obtain a clear solution. 0.15 ml. quantities of this solution are sparked for 40 seconds, the cadmium serving as internal standard.

### SUMMARY

1. The introduction of new techniques has improved the accuracy of certain spectrographic methods. Two such techniques of recent development are described, namely flame photometry and the "porous-cup" method, and these are considered sufficiently accurate for the determination of major as well as minor constituents in pharmaceutical materials.

2. The problems encountered in the application of these methods to the determination of certain elements in a number of pharmaceutical materials are described.

3. The given methods show a considerable saving of time over the normal chemical methods hitherto employed.

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DISCUSSION

The paper was presented by DR. D. C. GARRATT.

DR. F. HARTLEY (London) said that Dr. Garratt in his own way made the method sound simple, but in his propaganda for the spectrographic method he tended to minimise two aspects. One was the initial investigations of the interference by extraneous elements. It would be helpful if Dr. Garratt could say something about the influence of different anions on the determination of a particular cation. Secondly, it was to be hoped that the author would give some assistance in the future in assessing the proportion of impurities in cations by analytical methods. When revealed by emission spectrophotometric methods some shock might be sustained with regard to metallic impurities in preparations hitherto thought to contain a few parts per million.

DR. G. E. FOSTER (Dartford) pointed out that there were spectrophotometers available in which the lamp housing could be replaced by flame photometer accessories, and he asked the author whether such an arrangement would be suitable in a routine laboratory for use with both emission and absorption spectrophotometric problems. He was interested in the porous cup technique and enquired whether it was now possible to obtain silicon-free graphite electrodes.

MR. N. L. ALLPORT (London) asked whether the instruments manufactured for flame photometry, one in particular, were capable of doing the work which was described in the paper. The instrument described by Mr. Brealey some time ago appeared to be very elaborate and outside the possibilities of any but the largest firms. With regard to the question of precision, the actual method of flame photometry had such a sensitive reaction it meant that in calculating the results it would be necessary to multiply by a correction factor. He would like to hear whether precision could be maintained when using such very delicate reactions as sodium and potassium flame colours.

MR. M. DOMBROW (London) asked whether the authors had determined traces of impurities, particularly of lead, copper and zinc in magnesium trisilicate or other materials which were powerful absorbents. A problem which would have to be investigated was whether the large quantities of apparently harmful metallic impurities present in powerful absorbents were sufficiently released for them to be as dangerous as spectrophotographic figures might suggest.

DR. D. C. GARRATT, in reply, said that the techniques introduced were intended for routine work. With regard to the question of the cost of the instrument, when one considered the amount of time spent in chemical analysis, it was negligible. In answer to Dr. Hartley, the problem of

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anionic interference was overcome by various methods, and that subject had been dealt with by Mr. Brealey in a recent publication. Dealing with Dr. Foster's points, he had not used the photoelectric instrument for that work and, in fact, did not consider that it could be adapted for use in emission work. Pure graphite electrodes for the porous cup technique were now easily obtainable. No attempt had been made to work out trace elements in other absorbents than magnesium trisilicate.

MR. L. BREALEY, in reply, said that units were available for converting spectrophotometers into flame photometers. It was true that the ideal flame photometer was produced by adding a flame unit to the spectrophotometer in place of the lamp house. It would appear that Mr. Allport had the filter instrument in mind, but in his (Mr. Brealey's) opinion the only element which could be determined on a filter instrument with any precision was potassium. A monochromator should always be used for elements other than potassium. With regard to accuracy, highly dilute solutions were used with the flame photometer which gave the required precision. The fact that very dilute solutions were being used was a desirable feature of flame photometry.