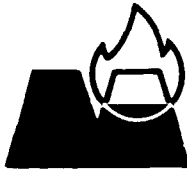


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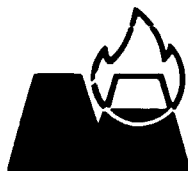
**AN ON-LINE DILUTION SYSTEM FOR SPECTROMETRY
USING AN INDUCTIVELY COUPLED PLASMA SOURCE**

by

G.L. Moore, A.E. Watson, and P.J. Humphries-Cuff

6th August, 1982

**COUNCIL FOR MINERAL TECHNOLOGY
200 Hans Strijdom Road
RANDBURG
South Africa**



MINTeK

(ANALYTICAL CHEMISTRY DIVISION)

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SYNOPSIS

An on-line dilution system that uses a two-channel peristaltic pump to feed a GMK Babington type of nebulizer is described. By the use of a diluent containing the appropriate concentrations of acid, sodium, and internal standard element, which was fed at a constant rate to the nebulizer, the system produced analytical results that are not significantly different (less than 3 per cent relative) from those obtained with the normal dilution technique. However, a considerable saving in time is achieved, as well as a saving in the use of expensive reagents.

SAMEVATTING

'n Inbaanverduunningstelsel wat van 'n peristaltiese tweekanaalpomp gebruik maak om 'n GMK-Babington-newelaar te voer, word beskryf. Met die gebruik van 'n verdunningsmiddel wat die gepaste konsentrasies suur, natrium en 'n interne standaardelement bevat, wat teen 'n konstante tempo in die newelaar ingevoer is, het die stelsel analitiese resultate gelever wat nie beduidend (minder as 3 persent relatief) van dié wat met die gewone verdunningstegniek verkry is, verskil nie. Daar was egter 'n groot besparing van tyd asook 'n besparing in die gebruik van duur reagentse.

CONTENTS

1. INTRODUCTION	1
2. EXPERIMENTAL METHODS	1
2.1. DESIGN OF AN ON-LINE DILUTION SYSTEM	1
2.2. OPERATING PARAMETERS	1
2.3. MIXING OF SAMPLE SOLUTION AND DILUENT	2
2.4. DETERMINATION OF THE DILUTION FACTOR	2
2.5. MEMORY EFFECTS AND WASHING-OUT TIMES	3
2.6. COMPOSITION OF THE DILUENT	4
2.7. TESTING OF THE DILUTION SYSTEM BY THE USE OF ROUTINE LABORATORY METHODS	5
2.7.1. Sulphide Concentrates	5
2.7.2. Ferromanganese Slag	6
3. DISCUSSION	6
4. CONCLUSIONS	7
5. REFERENCES	7

LIST OF TABLES

Table 1. Intensity readings and concentrations of copper, iron, and lead obtained with an integration time of 15 seconds	4
Table 2. Ratios of the intensities of the analyte to those of the internal standard, and the concentrations obtained with internal standardization	5
Table 3. Comparative results for the analysis of sulphide concentrates	5
Table 4. Comparative results for the analysis of ferromanganese slags	6

LIST OF ILLUSTRATIONS

Figure 1. The arrangement of the on-line dilution system	1
Figure 2. The effect of pump speed on the net signal-to-background ratios	2
Figure 3. Effect of pump speed on the reproducibility of mixing	3

1. INTRODUCTION

A very wide variety of mineralogical and metallurgical samples, in which the concentrations of the analytes vary from a few parts per million to very high percentages, are analysed in the laboratories of the Council for Mineral Technology (Mintek). In the Emission Spectroscopy Section, techniques involving inductively coupled plasma (ICP) sources are used extensively. If investigators are to cope with the wide range of analyte concentrations and to provide results of the highest accuracy and precision, they need to 'tailor' any particular method to cover a relatively restricted optimum calibration range that usually includes the lowest values expected.

As a result, certain elements in a multi-element method often exceed the calibration range used and necessitate the preparation of a diluted solution to bring them into the normal analytical range. The preparation of these diluted solutions containing the appropriate concentrations of acid, sodium (or other easily ionized element), and internal standard is time-consuming and wasteful of expensive reagents.

The description by Layman, Crock, and Lichte¹ of an on-line dilution system, which uses a multi-channel peristaltic pump to feed the nebulizer of an atomic-absorption spectrometer, prompted an investigation into the application of a similar system to the medium-powered nitrogen-cooled argon plasma used at Mintek. It was hoped that a procedure could be developed in which the solution would be delivered at a constant rate to the Babington type of nebulizer, thus avoiding the problems with the efficiency of nebulization that are usually associated with varying feed rates of solution.

2. EXPERIMENTAL METHODS

2.1. Design of an On-line Dilution System

A Gilson Minipuls 2 peristaltic pump with 10 rollers was used to feed a GMK nebulizer² supplying an aerosol to a medium-power (5 kW) ICP torch. Figure 1 illustrates the arrangement of the dilution system, in which a tube with a narrow bore is used for the sample-solution feed, and a larger tube for the diluent feed. Both tubes simultaneously deliver sample solution to the nebulizer for samples within the calibration range, and the larger tube is transferred to the diluent solution only where a dilution is necessary. Under these conditions, the rate at which the solution is fed to the nebulizer is constant, and the efficiency of nebulization remains unaltered.

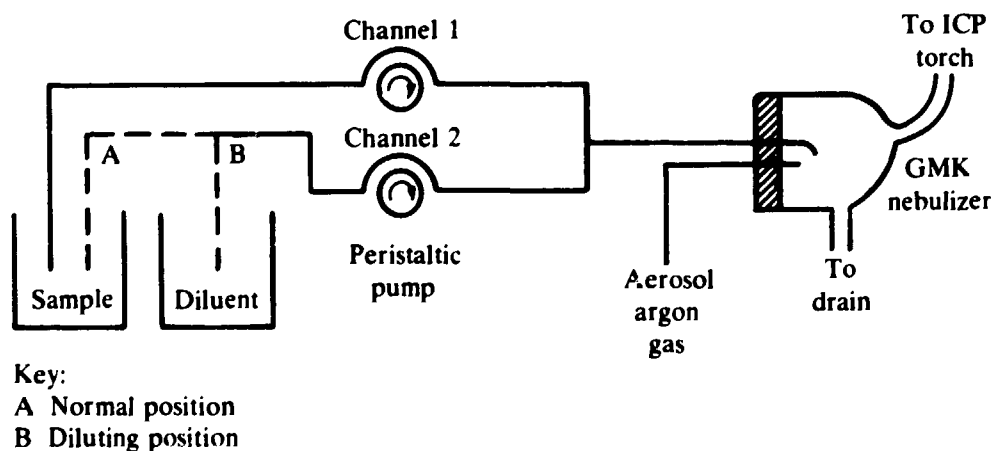


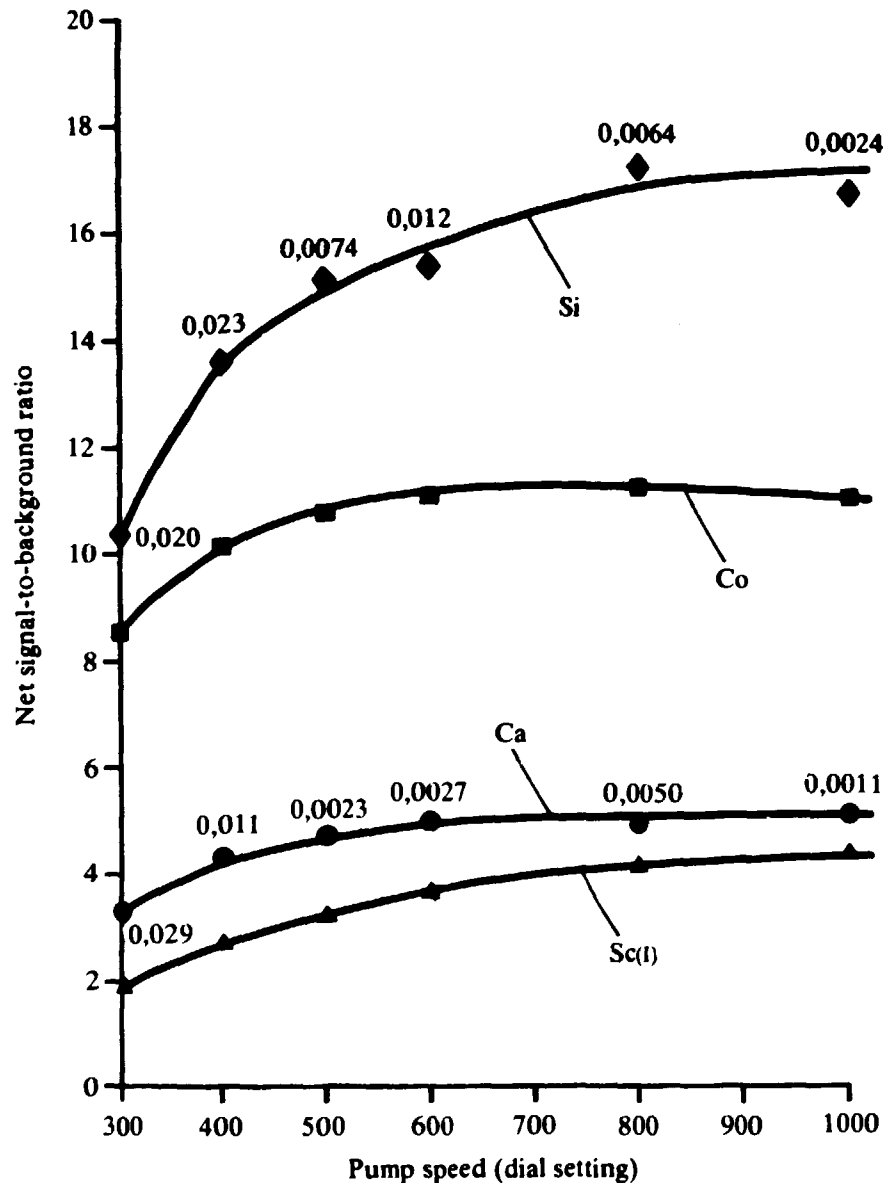
FIGURE 1. The arrangement of the on-line dilution system

2.2. Operating Parameters

The medium-powered nitrogen-cooled argon plasma was operated at the multi-element conditions determined as a compromise in a previous study³, except that, because the Meinhard concentric nebulizer was replaced by a GMK Babington type of nebulizer, an increased flowrate (1,6 to 1,8 l/min) of aerosol argon gas had to be adopted.

The effect of the speed of the pump on the precision of the background, the signal, and the net signal-to-background ratio (SBR) was investigated (Figure 2), and the optimum pump speed was found to be that indicated by a dial setting of at least 500 (equivalent to 5,00 ml/min). This speed would give high SBRs and high signal precision at a low feed rate of solution. The pump can be operated at maximum speed for washing-through.

DILUTION SYSTEM



Note: The figures given on the graphs are the s , values
(the precision of the signal is based on 10 readings)

FIGURE 2. The effect of pump speed on the net signal-to-background ratios

2.3. Mixing of Sample Solution, and Diluent

The reproducibility of the mixing of the sample solution and the diluent was tested at different pump speeds by the exposure of ten replicates of a multi-element solution containing concentrations within the normal calibration range. From Figure 3, it can be seen that the variability of the intensity readings, as represented by the relative standard deviation (s), decreases with increasing pump speed until it reaches a level that would be observed with a normal pneumatic nebulizer (s , 0,002 to 0,008).

A dial setting of 600 (equivalent to 6,1 ml/min) was selected for optimum operation to reduce the variations due to pulsing caused by the pump rollers and the mixing of the sample solution with the diluent. The effect of the pump speed on the net signal was also taken into account.

2.4. Determination of the Dilution Factor

Clearly, the dilution factor depends on the physical properties (wall thickness, elasticity, coefficient of thermal expansion, etc.) and the internal diameters of the tubing employed. The flowrates for various sizes of tubes were measured over periods of time of up to 1 hour. It was found that the flowrate increased

DILUTION SYSTEM

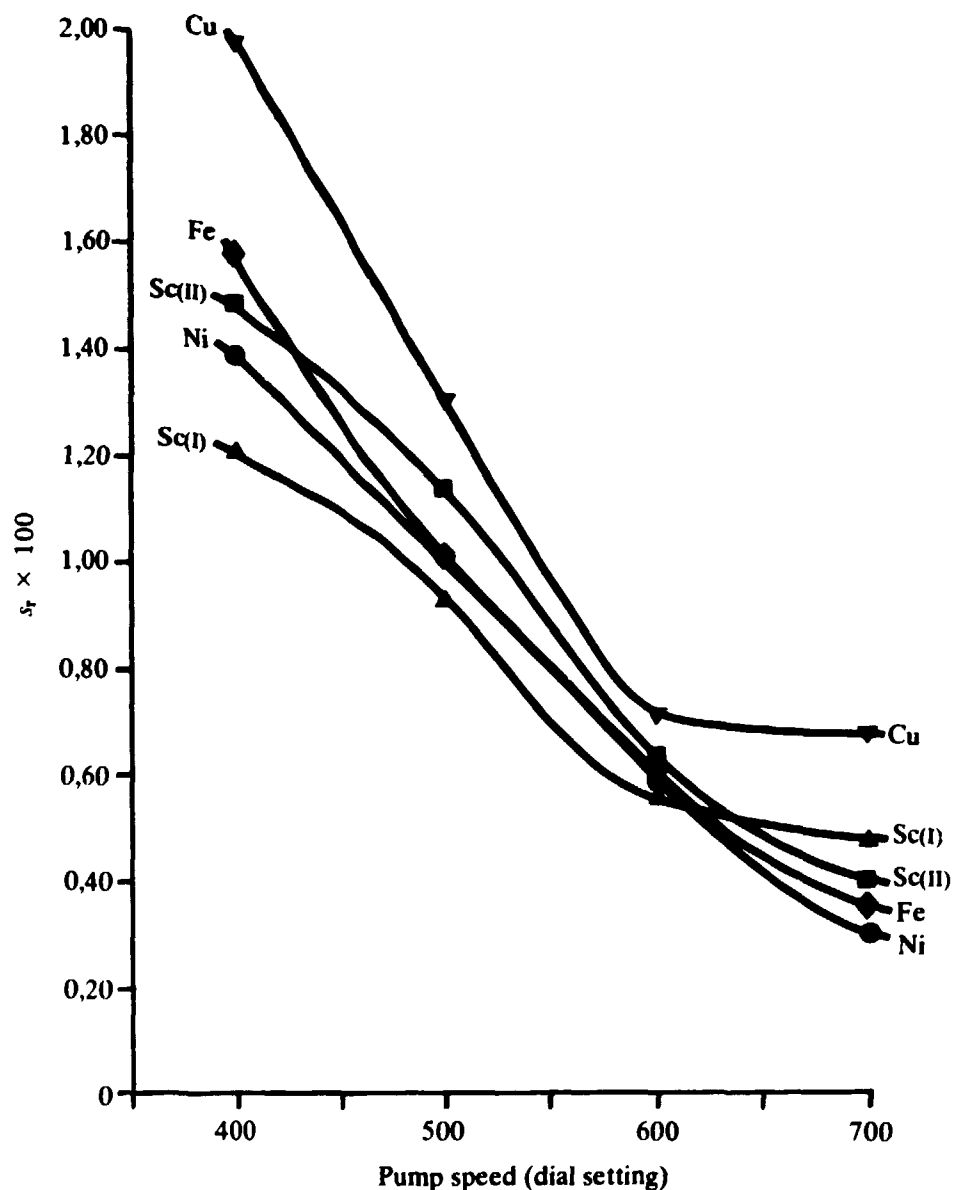


FIGURE 3. Effect of pump speed on the reproducibility of mixing

to a stable maximum in 15 to 20 minutes for all the tubes examined, which indicates that a warming-up time is required. The performance of a tube is then reproducible provided that the pressure-adjusting screw on that pump channel is not altered. However, an aging effect was observed, in that the performance of a tube becomes erratic after prolonged use and will not deliver a reproducible quantity of solution. This should be carefully monitored by measurement of the flowrate at regular intervals, and tubes should be changed before any appreciable alteration in precision is observed.

Since the objective was a dilution factor of approximately five, the tubing finally selected had internal diameters of approximately 1 mm (sample) and 3 mm (diluent). Calculations based on flow ratio showed that this system gave a dilution factor of 5.5. In practice, it was found that the dilution factor could be calculated from the reduction in concentration of the analytes that were determined within the normal calibration range, and a mean dilution factor was applied to those analytes needing dilution.

2.5. Memory Effects and Washing-out Times

The intensities of copper and iron were monitored on the profile meter, and, with the aid of a stopwatch, washing-out times were determined. When the on-line dilution system was not used (i.e., both the thick and the thin tube to be washed out), the washing-out time was 60 seconds at a pump speed of 600 (dial setting), reducing to 35 seconds at a pump speed of 1000 (maximum dial setting or over-ride switch). When

DILUTION SYSTEM

the on-line dilution system was used (i.e., only the thicker diluent tube to be washed out), the washing-out time was 35 seconds at a pump speed of 600 (dial setting), reducing to 20 seconds at the maximum pump speed.

2.6. Composition of the Diluent

For most of the investigative work, the diluent was matched to the sample solution with regard to the concentrations of acid, sodium, and the scandium internal standard, i.e., 50 mg/l in 10 per cent (v/v) hydrochloric acid. In an attempt to simplify the preparation of the diluent, which would result in the saving of time and money, six different diluents were prepared, one or more components being omitted from each diluent so that the effect of each of these components could be determined.

A routine method for the analysis of sulphide concentrates⁴ was used with the on-line dilution system in the analysis of an 'in-house' reference material (33/74) that contains copper, iron, and lead at levels well beyond the normal calibration range.

Intensity readings were obtained with a 15-second integration time for the copper, iron, and lead channels and for the two lines for the internal standard, Sc(I) and Sc(II). The intensity readings for the calibration standards were used in the construction of calibration graphs for copper, iron, and lead. The first of these was obtained without reference to the internal standard (Table 1); in the second, the ratios of the analyte intensities to the internal standard intensities were plotted (Table 2). These calibration graphs were linear, and were used in the derivation of the concentrations of copper, iron, and lead by multiplication with a dilution factor of 5,88 to give the concentrations (Table 1, and dilutions 1 to 4 in Table 2) or by extrapolation (dilutions 5 and 6 in Table 2).

TABLE 1

Intensity readings and concentrations of copper, iron, and lead obtained with an integration time of 15 seconds

Solution pumped to nebulizer	Composition of standard* or diluent	Cu(I) 324,754 nm		Fe(II) 259,940 nm		Pb(II) 220,351 nm		Sc(I) 402,040 nm	Sc(II) 255,237 nm
		Mean intensity mV†	Concn* %	Mean intensity mV†	Concn* %	Mean intensity mV†	Concn* %	Mean intensity mV†	Mean intensity mV†
Calibration standard 1	5% Cu, 5% Fe, 1% Pb	23 734	5	40 544	5	4 108	1	19 014	23 450
Calibration standard 2	3% Cu, 3% Fe, 5% Pb	14 416	3	24 904	3	17 944	5	19 096	23 568
Calibration standard 3	1% Cu, 1% Fe, 10% Pb	4 960	1	8 592	1	35 600	10	19 232	23 800
33/74 + diluent 1	HNO ₃ , NaNO ₃ , Sc, H ₂ O	16 632	(20,4)	27 936	(19,9)	10 664	(17,1)	18 680	23 232
33/74 + diluent 2	NaNO ₃ , Sc, H ₂ O	17 616	21,7	29 120	(20,7)	11 048	17,7	19 344	24 048
33/74 + diluent 3	HNO ₃ , - Sc, H ₂ O	17 224	21,2	31 440	22,5	12 264	19,8	19 528	26 000
33/74 + diluent 4	- - Sc, H ₂ O	18 608	22,9	33 848	24,3	13 248	21,5	20 560	27 632
33/74 + diluent 5	HNO ₃ , NaNO ₃ , - H ₂ O	16 480	(20,2)	28 128	(20,0)	10 912	(17,5)	5 112	4 296
33/74 + diluent 6	- - - H ₂ O	18 024	22,2	32 936	23,6	13 072	21,2	5 488	5 008
Tentative accepted value for 33/74		-	20,29	-	20,67	-	17,01	-	-

*Calculated on the basis of the original solid sample

† These readings correspond to mV × 6,552

Note:

The values in parentheses are within two standard deviations of the accepted value

From the results given in Tables 1 and 2, it is concluded that any departure in the composition of the diluents from that of the matrix of the sample solution (other than the omission of the internal standard) causes the values obtained to be significantly different from those recorded when the diluent and the sample solution are matched. This difference is most serious when the ratio of the analyte intensity to the internal-standard intensity is not used for the purposes of calibration. Without the use of the internal standard,

DILUTION SYSTEM

TABLE 2

Ratios of the intensities of the analyte to those of the internal standard, and the concentrations obtained with internal standardization

Solution pumped to nebulizer	Cu		Fe		Pb	
	Cu/Sc(II)	Concn* %	Fe/Sc(II)	Concn* %	Pb/Sc(II)	Concn* %
Calibration standard 1	1,012	5	1,729	5	0,1752	1
Calibration standard 2	0,6117	3	1,057	3	0,7614	5
Calibration standard 3	0,2084	1	0,3610	1	1,496	10
33/74 + diluent 1	0,7159	(20,7)	1,202	(20,2)	0,4590	(17,3)
33/74 + diluent 2	0,7325	21,2	1,211	(20,3)	0,4594	(17,3)
33/74 + diluent 3	0,6625	19,1	1,209	(20,3)	0,4717	17,8
33/74 + diluent 4	0,6734	19,4	1,225	(20,5)	0,4794	18,1
33/74 + diluent 5	3,836	(19,5)	6,547	(21,3)	2,540	(17,1)
33/74 + diluent 6	3,599	18,3	6,577	(21,4)	2,610	(17,6)
Tentative accepted value for 33/74		20,29	-	20,67	-	17,01

*Calculated on the basis of the original solid sample

Note:

The values in parentheses are within two standard deviations of the tentative accepted value

a positive bias of up to 4 per cent absolute was noted whereas, when the internal standard was used, no significant bias was observed and the values did not deviate from those obtained with matched diluent and sample solution by more than 1 per cent absolute. The use of atomic and ionic lines for scandium as the internal standards gave linear calibration curves, the degree of linearity showing that the Sc(II) line is a preferable monitor for the ionic lines for lead and iron as well as for the atomic line for copper.

2.7. Testing of the Dilution System by the Use of Routine Laboratory Methods

2.7.1. Sulphide Concentrates

By use of the optimum conditions referred to in Sections 2.2 and 2.3 and a matched diluent, the on-line dilution system was used with a method for the determination of the major elements in sulphide concentrates. The results obtained from solutions diluted ten times and those obtained by the on-line dilution method are given in Table 3.

TABLE 3

Comparative results for the analysis of sulphide concentrates

Reference material	Element	ICP value from solution diluted 10 times %	ICP value from on-line dilution method %
31/74	Zn	45,8	44,6
32/74	Pb	70,1	71,6
33/74	Cu	20,4	20,1
33/74	Fe	20,5	20,2
33/74	Pb	17,1	17,15

Note:

The maximum deviation between the normal and on-line dilution procedures does not exceed 2,7 per cent relative

2.7.2. Ferromanganese Slag

With the same optimum conditions as those described in Section 2.7.1, the on-line dilution system was used for the determination of manganese and silicon in an 'in-house' reference material¹ of ferromanganese slag. The preferred values⁶ for manganese oxide and silica, together with the corresponding results obtained from solutions diluted five times and the results obtained by the on-line dilution method, are shown in Table 4.

TABLE 4

Comparative results for the analysis of ferromanganese slags

Reference material	Replicate determination	Analyte	Accepted value	s	Results, %			
					Normal dilution method*	Mean	On-line dilution method	Mean
34/69	A	SiO ₂	26,74	0,36	27,7	27,6	28,0	27,6
	B				28,0		27,5	
	C				27,0		27,4	
35/69	A	SiO ₂	48,30	0,42	49,0	49,2	49,1	49,7
	B				49,3		49,6	
	C				49,4		50,3	
36/69	A	MnO	41,74	0,89	41,7	41,4	41,2	40,4
	P				41,6		40,1	
	C				41,0		40,1	
36/69	A	SiO ₂	26,79	0,42	27,2	27,3	26,9	26,9
	B				27,1		26,6	
	C				27,6		27,2	

*Solution diluted 5 times

Note.

The maximum difference between the values obtained with the normal and on-line dilution procedures does not exceed 2,5 per cent relative

3. DISCUSSION

The preliminary work recorded here showed that the on-line dilution system can be used for dilutions of up to five times, and the mixing reproducibility was found to be satisfactory up to a dilution factor of 10. Layman, Crock, and Lichte¹ report mixing problems at factors greater than 20.

It had been hoped that, if one omitted the internal standard from the diluent, thus effecting a saving in expensive reagent, an accurate result for concentration would be obtained via the microprocessor. Such a result would obviate the need for a dilution factor to be determined as well as the need for final manual multiplication by this factor. Tables 1 and 2 show that accurate results were obtained, irrespective of whether the internal standard was included in the calculation or not.

Unfortunately, although this short-cut method to yield accurate results was valid in this particular instance, it has no universal applicability. This serious drawback needs to be explained in some detail.

When the internal-standardization mode is used, the computer programme in use compares the intensity reading for scandium with a pre-set value and makes a proportionate adjustment to the intensity reading for the analyte. If the scandium intensity drops by a factor of 5, the analyte reading increases fivefold, and this inflated reading is used in the calculation of the concentration by extrapolation from the calibration curve. Provided that the calibration curve is linear over this extended range, the extrapolated value should be accurate, but it is clear that the accuracy will be adversely affected in most instances and that, if the calibration graph is curved (as it normally is for such elements as magnesium, zinc, etc.), the extrapolated result will be far from accurate. One reason for this inaccuracy is that the computer stores a curve in memory as a series of chords, and extrapolates by producing the final chord to the required length.

Omission of the acid from the diluent caused the nebulization properties to alter, whereas omission of the sodium led to changes in intensity that might have been caused by a change in the nebulization properties, and were almost certainly due to ionization effects in the plasma. Neither of these omissions could be adequately compensated for by the use of internal standardization. The omission of the internal

standard from the diluent yielded accurate results, irrespective of whether the results were calculated on the basis of internal standardization or not. The acceptable accuracy obtained in the calculation based on internal standardization was due to the large range in linear calibration of the three particular elements involved.

For routine work involving the use of an internal standard, the diluent should contain the appropriate amount of internal standard, thus maintaining the ratio of analyte to internal standard within the normal calibration range. The accuracy of the results will be far greater than that obtained with extrapolation (i.e., when the internal standard is missing from the diluent). In this instance, the accuracy is very dependent on the linearity of the calibration graph.

In the light of the limited work carried out so far, the method yielded results of satisfactory accuracy with a precision comparable with that obtained by the normal dilution technique. The deviation between the normal and the on-line dilution procedures does not exceed 3 per cent relative, whereas the maximum deviation from the accepted values (based on the work of 13 laboratories) does not exceed 3 per cent.

As far as the implementation of the method on a routine basis is concerned, the operator would need to exercise more care than usual for the following reasons:

- (a) there are two tubes to manipulate,
- (b) the washing-out time is marginally longer, and
- (c) there is a higher possibility that bubbles will be trapped in the system, which could cause variation in the dilution factor.

These potential problems can be minimized by clear identification of the tubes (by the use of colours perhaps), the building of a suitable pre-spark time into the measuring system, and by ensuring that the delivery tubes between the pump and the nebulizer are 'up-hill', i.e., the pump outlets should be below the level of the intake port of the nebulizer solution.

An unforeseen benefit of the method is the considerable reduction in the pulsing effect of the pump as a result of different sizes and lengths of sample and diluent tubes from the pump to the T-piece.

For a routine method in which 50 per cent of the samples require a diluted solution to be prepared, the saving in time would amount to approximately 10 per cent of the total analysis time. If all the samples are received in solution requiring dilution, the saving in time can amount to 40 per cent.

4. CONCLUSIONS

An on-line dilution system requiring a two-channel peristaltic pump feeding a GMK Babington type of nebulizer was constructed and tested successfully by the use of two routine laboratory methods. The main innovative feature of the technique is the provision of a constant feed rate of solution to the nebulizer, which eliminates the variation in nebulization efficiency that results from different feed rates.

An optimum pump speed was determined, account being taken of signal stability, net signal-to-background ratios, and the rate of the total sample uptake. Analytical results of satisfactory accuracy were obtained for several reference materials containing elements at high concentrations.

A diluent that is not matched to the sample solution in terms of its concentrations of acid, sodium, and internal standard might give less accurate results.

Although the implementation of this on-line dilution system on a routine basis would require a little more attention from the operator, it would bring benefits in the form of substantial savings in the use of scandium internal standard and in the time spent on the preparation of dilutions.

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