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A DIRECT READING SPECTROMETER FOR THE DETERMINATION OF BERYLLIUM IN SITE LIQUID EFFLUENT

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ABSTRACT

This report describes a single channel direct reading spectrometer for the determination of beryllium in liquid effluent samples from delay tanks on the site of the Australian Atomic Energy Commission's Research Establishment. The rotating disc technique with pulsed arc excitation is used to determine beryllium down to 0.1 p.p.m. The limit of detection is 0.01 p.p.m. and the coefficient of variation at the 0.1 p.p.m. level is ± 20 per cent for a 95 per cent confidence level.

The beryllium intensity is depressed by the presence of other constituents in the effluent. Calibration is therefore carried out with standards prepared from a composite effluent solution which yields a similar depression of the beryllium intensity. The results are biased for different tanks and range from + 20 per cent to - 10 per cent.

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ABSTRACT (Continued)

The nature of the depression of the beryllium intensity has been studied in relation to the interference effects of foreign anions and cations and the sensitivity of the method is shown to be affected by pH and by the grade of graphite discs used.

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1. INTRODUCTION

A rapid method was required to determine beryllium in liquid effluent from various delay tanks prior to sludge blanket treatment and subsequent discharge. Because of the large number of these samples requiring analysis, it was decided to construct a direct reading spectrometer based on a spectrographic method previously used (Dixon - A.A.E.C. unpublished). Basically the instrument was required to process samples rapidly with little or no sample preparation, and to detect beryllium at the 0.1 p.p.m. level in the effluent solutions.

Most components of the instrument are available commercially.

2. DESCRIPTION OF INSTRUMENT

2.1 General

The electrode system is a rotating disc enclosed in a ventilated housing. Light from the pulsed arc discharge is focussed by a lens onto the slit of a monochromator which is set to isolate the Be 3130.42 Å line. The wavelength alignment is set by focussing the output of a beryllium hollow cathode lamp onto the slit of the monochromator. A photomultiplier at the exit slit amplifies the signal and this is fed to an integrating condenser bank. After the termination of the preset exposure period, the voltage on the condenser bank is read on a vacuum tube voltmeter. This voltage is translated to concentration of beryllium after precalibration with standard solutions. Figure 1 is a block diagram of the instrument, and Figure 3 shows the optical layout.

2.2 Monochromator

The monochromator is of the Ebert type and its performance and components are as follows:

Model : S1-RO-SPEC Model M1
(Techtron Pty. Ltd. Melbourne, Australia)

Focal Length : 0.5 m.

Grating : 50 mm x 50 mm ruled area; 600 lines per mm.

Slits : Kinematic, set at 5 μm.

Reciprocal Linear Dispersion : 16 Å/mm (second order).

Speed : f/10.

Figure 2 shows the resolution of the beryllium doublet (Be 3130.42 Å and 3131.07 Å) using the above conditions.

2.3 Electrode Assembly

The rotating disc assembly is constructed of stainless steel and Perspex and is generally similar to that manufactured by Jarrell-Ash Co., U.S.A. The porcelain boat is raised into position with a sliding platform, where a stop ensures that the disc (Ringsdorff Form RW1) maintains a constant solution depth. A motor coupled to the disc shaft rotates the disc at 15 rev/min in an anti-clockwise direction with reference to left-to-right optics. The upper electrode is a $\frac{1}{4}$ in.dia. graphite rod (National AGKS grade) shaped to a 120° cone on the end and is held in position by a spring clip. The gap (2 mm) is set with a spacer. When the electrodes are in position and the gap is set the image of the gap formed by a spherical lens is located centrally on the slit face of the monochromator.

2.4 Excitation Source

A pulsed-arc type discharge is used to excite the spectrum and produces half sine wave pulses of 10 amp peak current and 1 millisecond duration at a repetition rate of 50 pulses per second (Whittem 1962). The exposure is controlled by a timer (Rodene 7000) which is initiated when the source is activated and switches off the source after a preset time.

2.5 Detector

An E.M.I. photomultiplier Type 6256A is used to amplify the signal. The use of this detector necessitated redesigning the photomultiplier housing of the monochromator. The dynode voltages are supplied by a Philips power supply Type PW4024/01. The linearity of the output of the detector is improved by replacing the first, twelfth and thirteenth dynode resistors with 150 volt 5 watt Zener diodes (Type $\frac{1}{4}$ M150Z Motorola) (Budde 1965).

A grounded μmetal shield, suitably insulated from the glass envelope of the detector, eliminates instabilities in the output of the photomultiplier brought about by radio frequency interference from the source.

2.6 Integrating Condensers

The condenser bank consists of five Styroseal condensers each 3.3 μF at 125 volts working voltage. These are used for their low leakage and dielectric relaxation characteristics.

2.7 Readout

The integrated voltage is read on a vacuum tube d.c. microvoltmeter (Philips GM6020/03).

2.8 Control Unit

The control unit houses the condenser bank and a switch on the front panel determines the mode of operation. For analysing samples the switch is in the INTEGRATE position. For wavelength alignment it is turned to the DIRECT READING position. The operating sequence is controlled by two relays. In the INTEGRATE position, the output from the photomultiplier is connected to the integrating condensers and one relay isolates the voltmeter from the condensers during the exposure. The other relay, a pneumatic time-delay type, discharges the condensers during the first second of the exposure. In the DIRECT READING position the output of the photomultiplier is connected through a relay direct to the voltmeter. The switch isolates the condenser bank in this position. A discharge button is also provided for manually shorting the condensers.

3. CALIBRATION

3.1 Preparation of Standards

Standards in the range 0.1 to 1.0 p.p.m. were prepared by dilution of a master beryllium sulphate solution. Figure 4 is a typical calibration obtained with these standards.

During the processing of samples it was noted that the pH varied between 5 and 9. The beryllium present in alkaline solutions would hydrolyze, causing precipitation and yielding inhomogenous sampling. The effect of pH was therefore investigated by adjusting 0.1 and 0.5 p.p.m. standards to various pH values over the range 2 to 10. Figure 5 shows the effect of varying pH and indicates that the region between pH 4 and 6 yields maximum intensity. In more acidic solutions the beryllium intensity is severely depressed and in more alkaline conditions the depression is not so drastic. As a result of this pH dependence, it was evident that the calibration required standardization with respect to pH, and that for maximum sensitivity both samples and standards would require adjustment to the pH 4 to 6 range. A check was made on the pH of the standards used to obtain the calibration in Figure 4 and it was found that the values ranged between pH 4 and 5. This calibration therefore gives a true relationship between signal and concentration and is not affected by variable sensitivity due to pH.

This acidity effect was investigated on the blank. No variation occurred, indicating that it is associated only with the beryllium emission.

To test the consistency of the calibration with the samples, standard additions were made to blank effluent samples. These indicated that the beryllium intensity in the samples was depressed relative to the standards. The depression was presumed to be brought about by the presence of other constituents such as detergents, soaps and various anions and cations. These other constituents are present in indeterminable amounts and, rather than attempt to approximate the composition synthetically, a composite blank effluent sample was taken and standards were prepared from this. This method of standardization was checked by standard additions to various samples and was shown to be fairly consistent with these. For some samples the standard additions did not agree with the calibration, indicating that a matrix effect existed between samples. The matrix effect for a particular holding tank could be expected to vary rapidly with time and it was therefore necessary to carry out a survey on the consistency of the calibration with the samples over a period of time. This was accomplished by making standard additions to samples from representative tanks, and comparing these with the composite standard. Table 1 is a summary of the results obtained over a 30 day period. The results are expressed as the ratio of the mean value of the sample plus 0.1 p.p.m. Be, to the mean value of the other 0.1 p.p.m. Be composite standard obtained on the same day.

Applying the t-test of significance to these results it was found that, for a 95 per cent probability, no significant difference occurred for Tanks 2 and 3. Tanks XI and RN were significantly different and the per cent bias for each was + 20 per cent and - 11 per cent respectively.

These figures show the variations which occur over a limited period of time and it is not implied that they hold or may represent the composition of a particular tank at all times. To confirm the calibration, it is necessary to check, by standard addition, the consistency of the calibration with samples from the various tanks from time to time.

4. CHEMICAL INTERFERENCES

A study of interferences was made to account for the observed suppression of beryllium in the samples. This survey was limited to a selection of anions and cations and did not include soaps, detergents and other organic material which may be present in the effluent.

4.1 Effect of Cations

4.1.1 Blank

The effect of cations on the blank was investigated. The results are summarized in the Table 2.

Ti and V were selected to observe the extent of spectral line interference from these elements (Ti 3130.8 Å II, Ti 6261.099 Å I and V 3130.267 Å II). For Ti at the 100 p.p.m. level no appreciable increase in signal was observed whereas the presence of 500 p.p.m. V gave rise to a small but insignificant increase.

4.1.2 Standards

A similar study was carried out to observe the effect of extraneous cations on the beryllium intensity. Aliquots of a 0.1 p.p.m. Be standard in the presence of varying concentrations of a selection of cations were taken. The cations chosen were the major constituents present in the effluent found by spectrographic analysis of a number of samples, namely, Na, Ca, Al and Mg. K, Cr and Cu were also tested.

Interference from Al, Mg and Ca is shown in Figure 6. Na, K, Cr and Cu exhibited no interference effects at the 1,000 p.p.m. level.

From the figure, much of the depression in the beryllium intensity in the effluent can be attributed to the presence of Al, Mg and Ca.

4.2 Effect of Anions

4.2.1 Blank

Blanks were prepared by adjusting the pH of demineralized water to 4 with HNO_3, H_2SO_4, H_3PO_4 and HF. No decrease in signal occurred when these solutions were compared with water acidified to pH 4 with HCl.

4.2.2 Standards

Aliquots of a 0.1 p.p.m. Be standard were adjusted to pH 4 with the same acids. HNO_3 and H_2SO_4 yielded no decrease in signal, but severe depression occurred with H_3PO_4 and HF.

4.2.3 Phosphate ion

The extent of the interference due to this ion was investigated by observing the signals for 1, 10 and 100 p.p.m. PO_4^{3-} added to a 0.5 p.p.m. Be standard. Figure 7 shows that the interference extends down to 1 p.p.m. PO_4^{3-} .

4.2.4 Fluoride ion

The effect of fluoride ion was tested over a wide range of concentration. Figure 8 illustrates the effect for 0.1 to 100 p.p.m. F^- added and shows the interference to extend down to about 0.1 p.p.m. F^- .

These interferences observed for phosphate and fluoride are probably due to the formation of stable complexes with beryllium. These complexes are more difficult to excite, resulting in lower sensitivity. It is known that the fluoride complex is more stable than the phosphate complex and this is borne out by the relative depression effects of the two ions.

5. USE OF VARIOUS GRADES OF GRAPHITE

5.1 Comparison of Graphite Discs

Sensitivity was compared for three different grades of graphite discs, Ringsdorff RW1, National AGKSP and Morganite. The counter electrode was National AGKS rod in all cases and blank readings for each type were:

Ringsdorff	48 mV
National	43 mV
Morganite	39 mV

A series of exposures were made on each type selected at random and the sensitivity was tested at the 0.1 p.p.m. Be level. The results, expressed as a mean of all exposures made on each type were:

Ringsdorff	354 mV
National	216 mV
Morganite	178 mV

These results indicate that, to achieve maximum sensitivity with this method, the choice of graphite disc is critical.

The sensitivity for used Ringsdorff discs was also tested. Those discs for which blank readings had previously been obtained were selected. They were washed several times in demineralized water and dried, since it had been observed that successive exposures of a disc without such treatment yielded a decrease in sensitivity.

The value of the blank then obtained was 46 mV and the signal for 0.1 p.p.m. was 369 mV. The sensitivity for these used discs is similar to that of the unused type.

A comparison of counter electrodes was also made for Ringsdorff RWI, National AGKS and AGKSP grades of graphite rod using the Ringsdorff discs. The sensitivity was found to be unaffected from one grade to another indicating that the choice of counter electrode was not critical.

5.2 Greased Discs

Greasing of rotating discs with a solution of Apiezon grease in petroleum ether (~ 1 g/litre) has been used to reduce blanks (U.K.A.E.A. 1963) and remove variable porosity effects. A comparison was made of sensitivity and coefficient of variation for greased and ungreased discs. At the 0.1 p.p.m. Be level, the mean readings for greased and ungreased discs were 120 and 181 mV respectively and the coefficients of variation were 10 per cent and 13 per cent respectively. This slight improvement in the coefficient of variation for greased discs was considered to be of no real advantage in view of the poorer sensitivity obtained.

6. DISCUSSION

The determination of beryllium using this technique is affected by many factors. The sensitivity depends on pH, the range pH 4 to 6 yielding a broad maximum of sensitivity. The standards are adjusted to pH 4.5 to prevent hydrolysis of the beryllium. By adjusting the pH of samples containing beryllium to the range pH 4 to 6, the results are consistent with the calibration.

Standard additions to representative tanks reveal that a matrix effect exists which varies from tank to tank and even within a particular tank over a period of time. By calibrating the instrument with standards prepared from a composite blank effluent solution, a fairly consistent calibration is obtained. Results for some tanks are, however, still biased.

The matrix effect results from the presence of foreign anions and cations. Suppression by Al, Ca and Mg occurs for concentrations greater than 1 p.p.m. for Ca and Mg and greater than 0.1 p.p.m. for Al. The concentrations of these interfering cations within a particular tank vary, resulting in a variable matrix effect. These variations have been shown to lie within acceptable limits and hence a single calibration is suitable. Since only short term effects have been investigated it is necessary to confirm the consistency of the samples and standards from time to time by standard additions to representative samples.

Phosphate and fluoride also interfere. Suppression due to phosphate occurs above 1 p.p.m. whilst for fluoride it occurs above 0.1 p.p.m. The suppression is presumably due to the formation of stable complexes with beryllium which are not easily excited in the discharge.

Since the samples are analyzed directly with no sample preparation, another factor which can yield erroneous results is the presence of beryllium in the form of particulate matter (generally as the oxide). However, provided the sample is shaken vigorously before sub-sampling, the method does detect the presence of beryllium in this form. Such samples generally give rise to a wide spread of readings for a number of exposures. The result obtained, although subject to a large error, is nevertheless satisfactory for effluent control.

Large variations in sensitivity are obtained with different grades of graphite discs. The type of counter electrode is not critical. Although it has been established that discs may be re-used, this practice has not been followed owing to the time involved in their preparation. Successive exposures of discs without treatment yield a decrease in sensitivity. Greased discs, while yielding a marginal increase in coefficient of variation, also decrease the sensitivity. For this reason discs are not greased.

Improvements to the method by way of possible elimination of the matrix effect and achievement of homogeneous sampling would require sample preparation involving acid digestion (U.K.A.E.A. 1963). This tends to defeat the purpose of establishing a rapid method for processing large batches of samples.

7. ACKNOWLEDGEMENTS

Thanks are due to Mr. C. Matulis for his helpful assistance and to Mr. R. N. Whittem for suggestions on design features of the instrument.

8. REFERENCES

Budde, W. (1965). - Applied Optics, 3 : 69.
U.K.A.E.A. (1963). - PG Report 496(S).
Whittem, R. N. (1962). - AAEC/M63.

TABLE 1

STANDARD ADDITIONS TO VARIOUS TANKS OVER A PERIOD OF 30 DAYS

Day	Ratio = $\frac{\text{Value of sample + 0.1 p.p.m. Be added}}{\text{Value of 0.1 p.p.m. Be standard}}$			
	Tank 2	Tank 3	Tank XI	Tank RN
1	1.09	1.03	1.34	-
2	0.98	0.96	1.39	0.79
3	1.00	0.98	1.26	0.92
4	1.49	0.68	-	1.01
5	1.10	0.95	1.03	-
6	0.92	1.15	-	0.96
7	1.03	1.05	0.94	0.92
8	0.95	0.88	-	0.83
9	-	0.76	1.47	0.70
10	1.03	1.13	1.21	0.99
11	0.86	1.00	-	0.94
12	0.94	0.98	1.13	0.81
13	0.80	-	0.98	0.88
14	0.70	-	1.25	0.91
Mean	0.99	0.96	1.2	0.89
Mean of all ratios = 1.002				

TABLE 2

EFFECT OF CATIONS ON BLANK

Cation	Concentration (p.p.m.)	Reading (mV)
Nil (demin. water)	-	50
Al	1,000	48
Ca	1,000	49
Cu	500	49
Cr	1,000	50
K	1,000	44
Ti	1	48
Ti	10	51
Ti	100	50
V	500	65
Mg	1,000	54

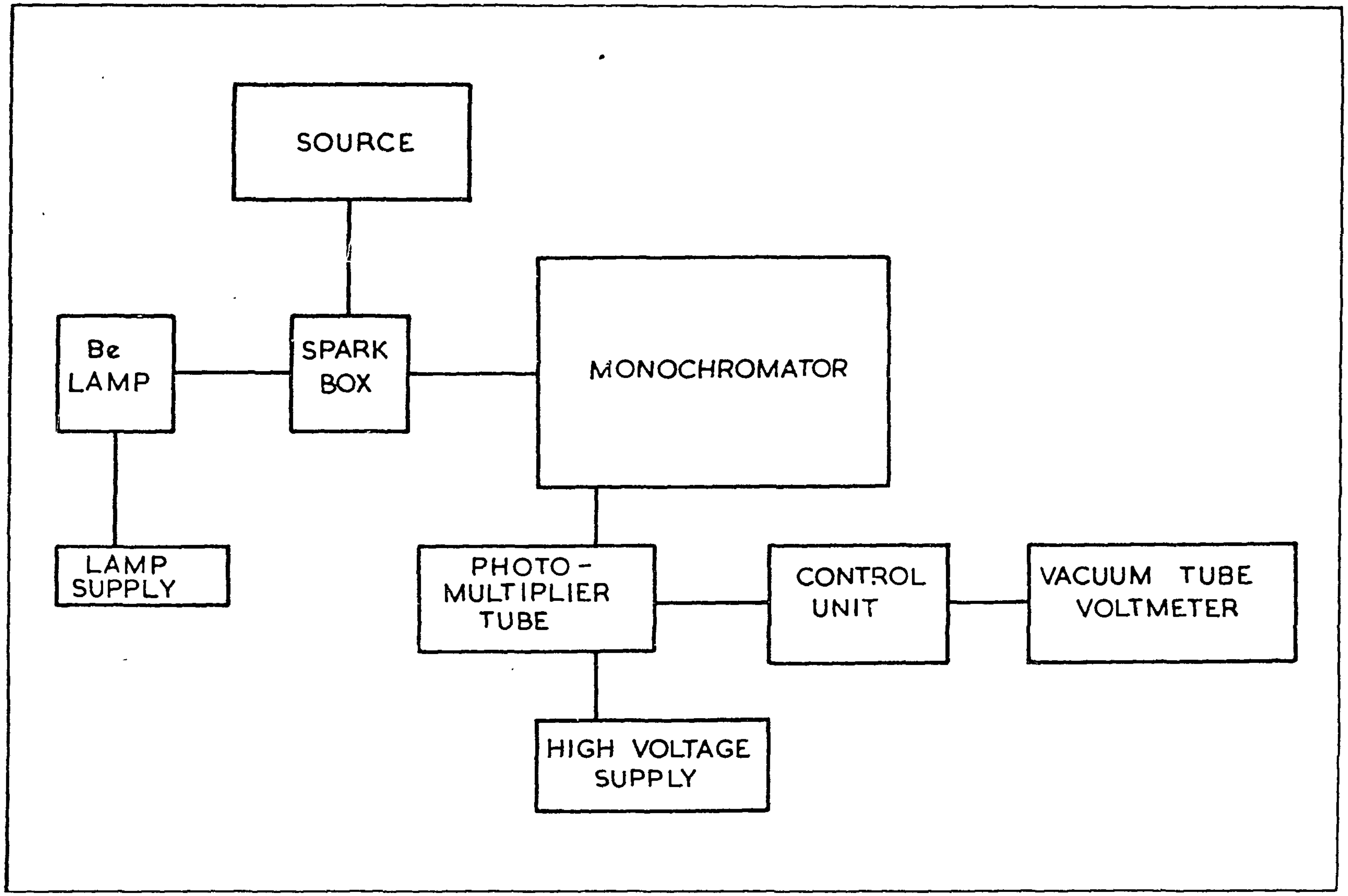

FIGURE 1. BLOCK DIAGRAM OF SPECTROMETER

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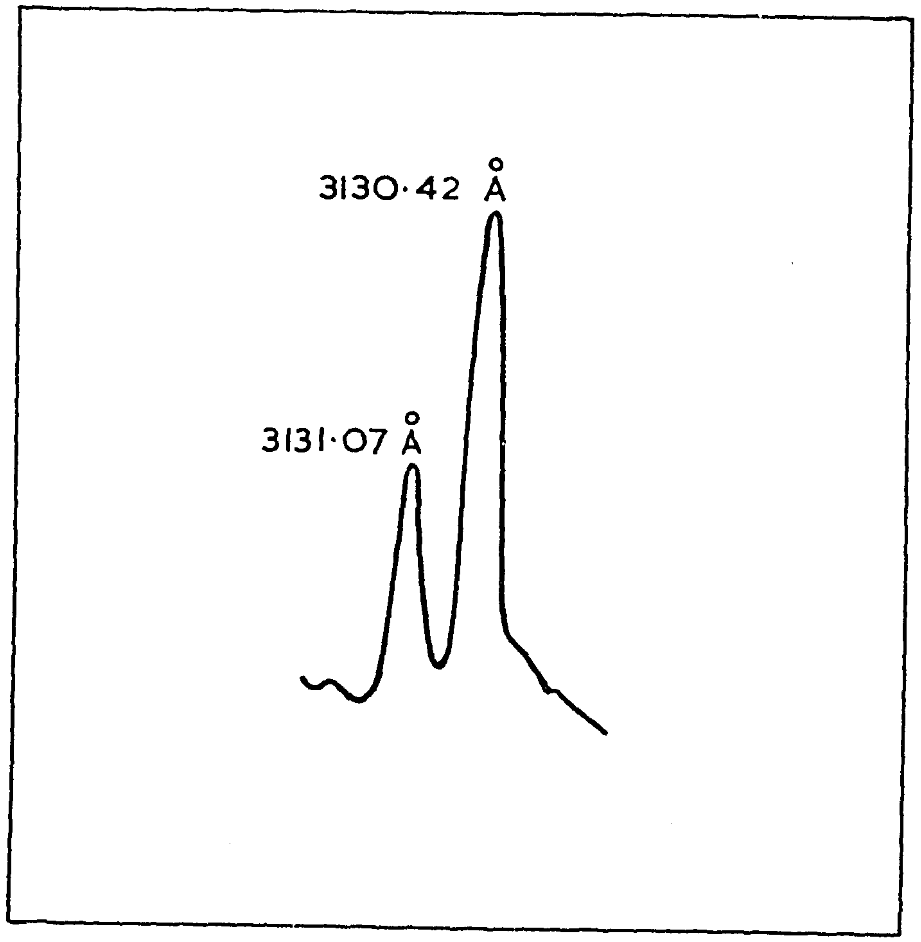

FIGURE 2. RESOLUTION OF BERYLLIUM DOUBLET

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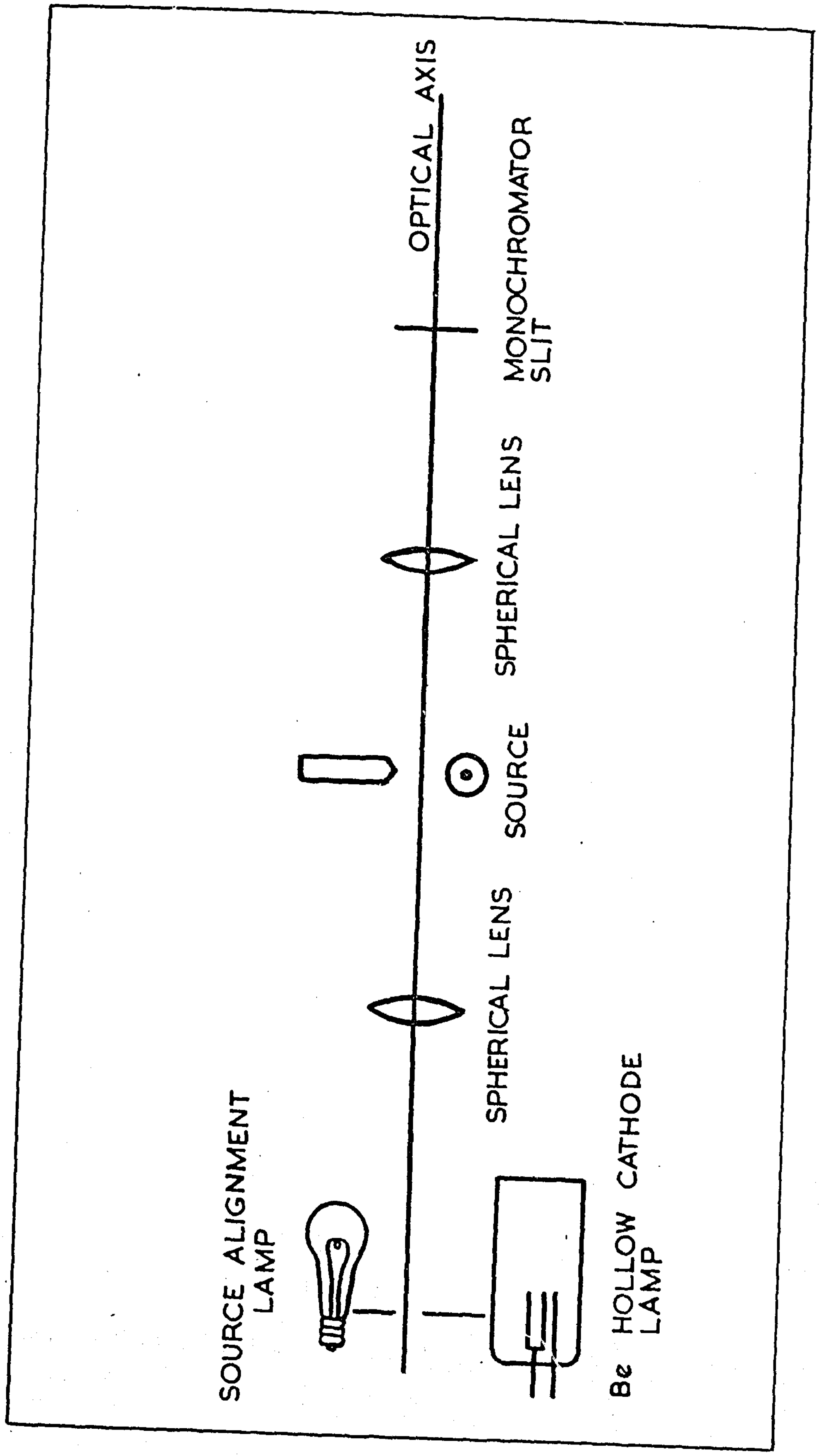

FIGURE 3. OPTICAL LAYOUT FOR WAVELENGTH ALIGNMENT AND SOURCE ALIGNMENT

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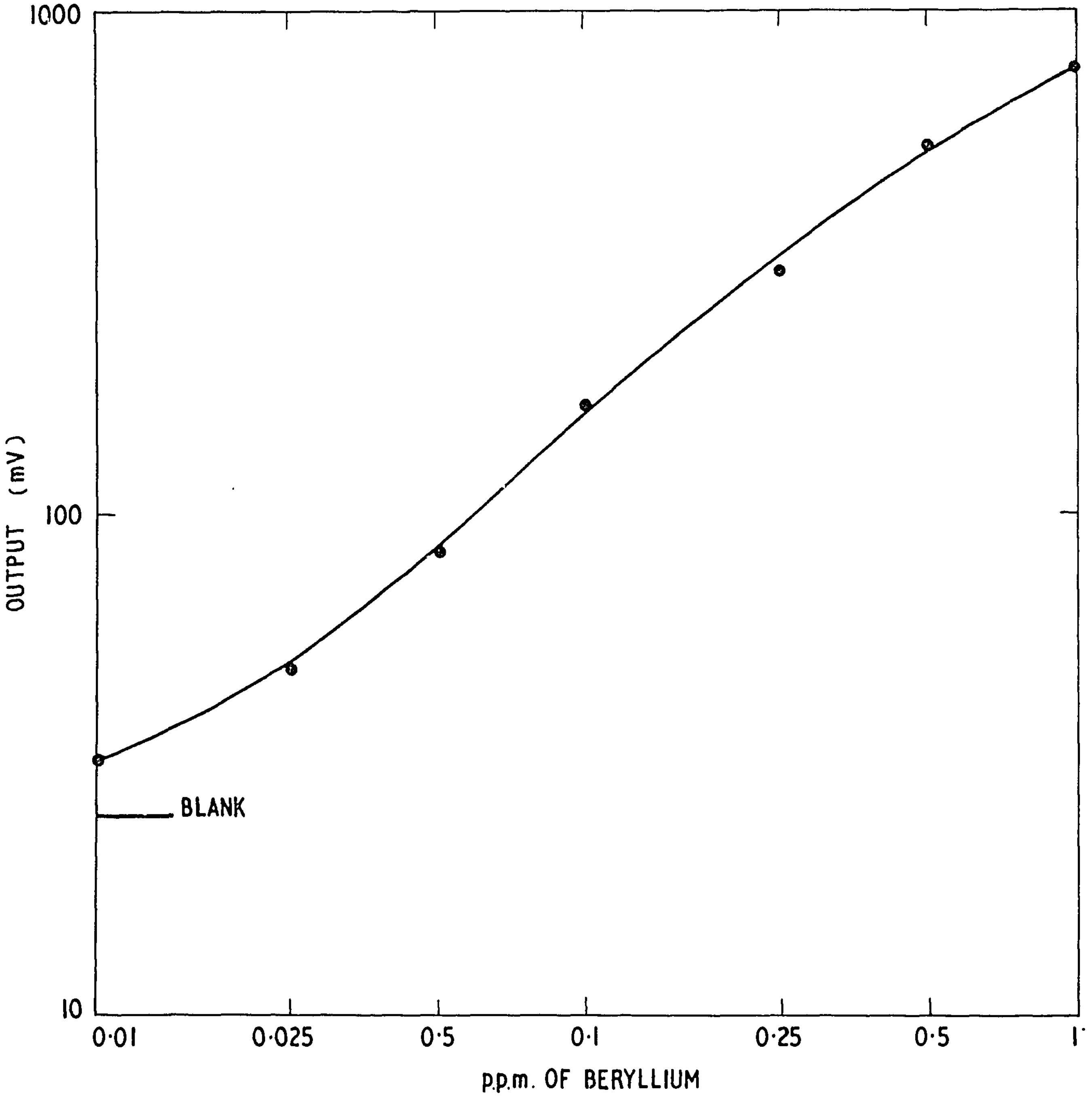

FIGURE 4. TYPICAL CALIBRATION FOR DIRECT READING SPECTROMETER

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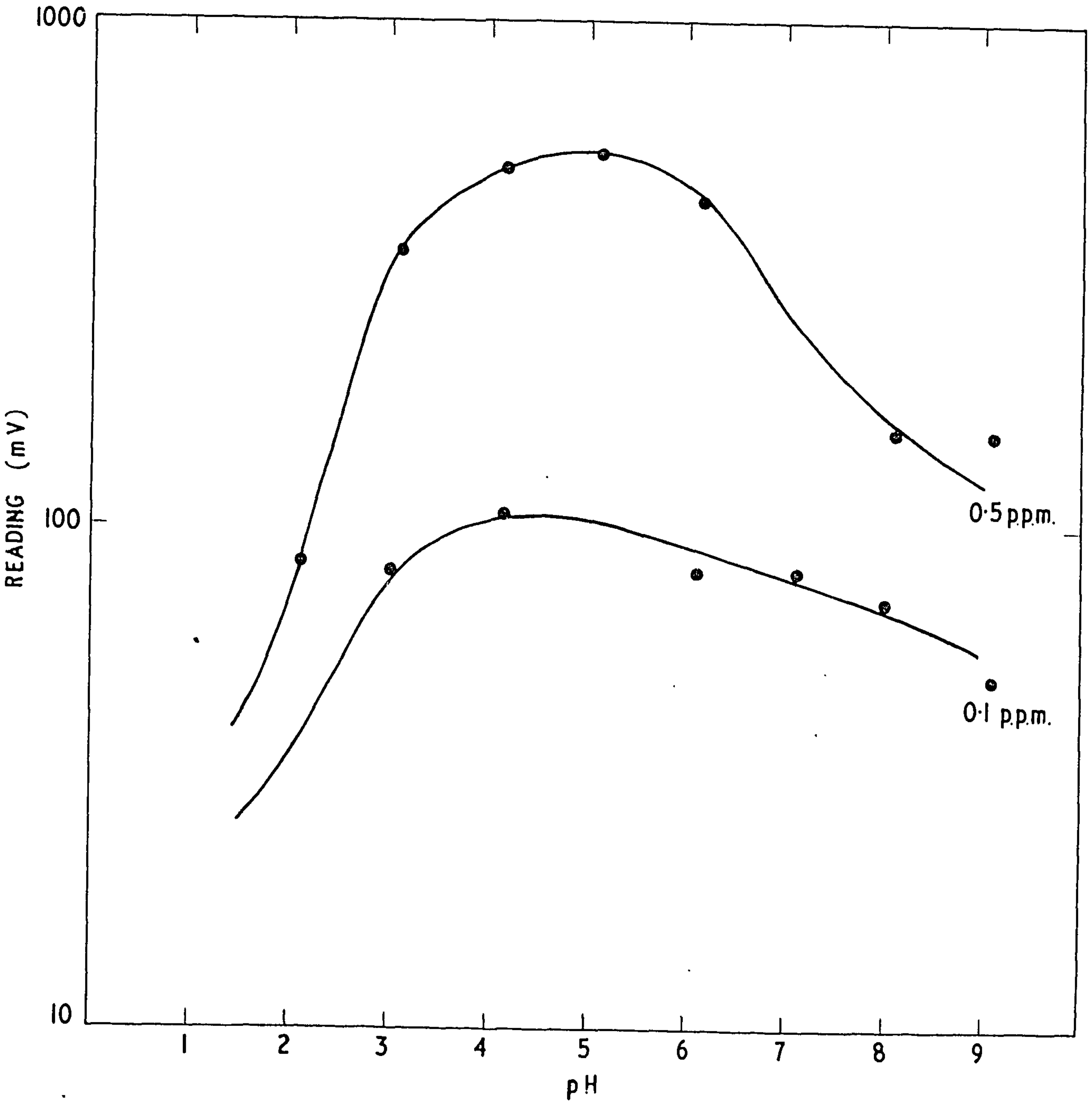

FIGURE 5. EFFECT OF ACIDITY ON 0.1 p.p.m. AND 0.5 p.p.m. Be SOLUTION

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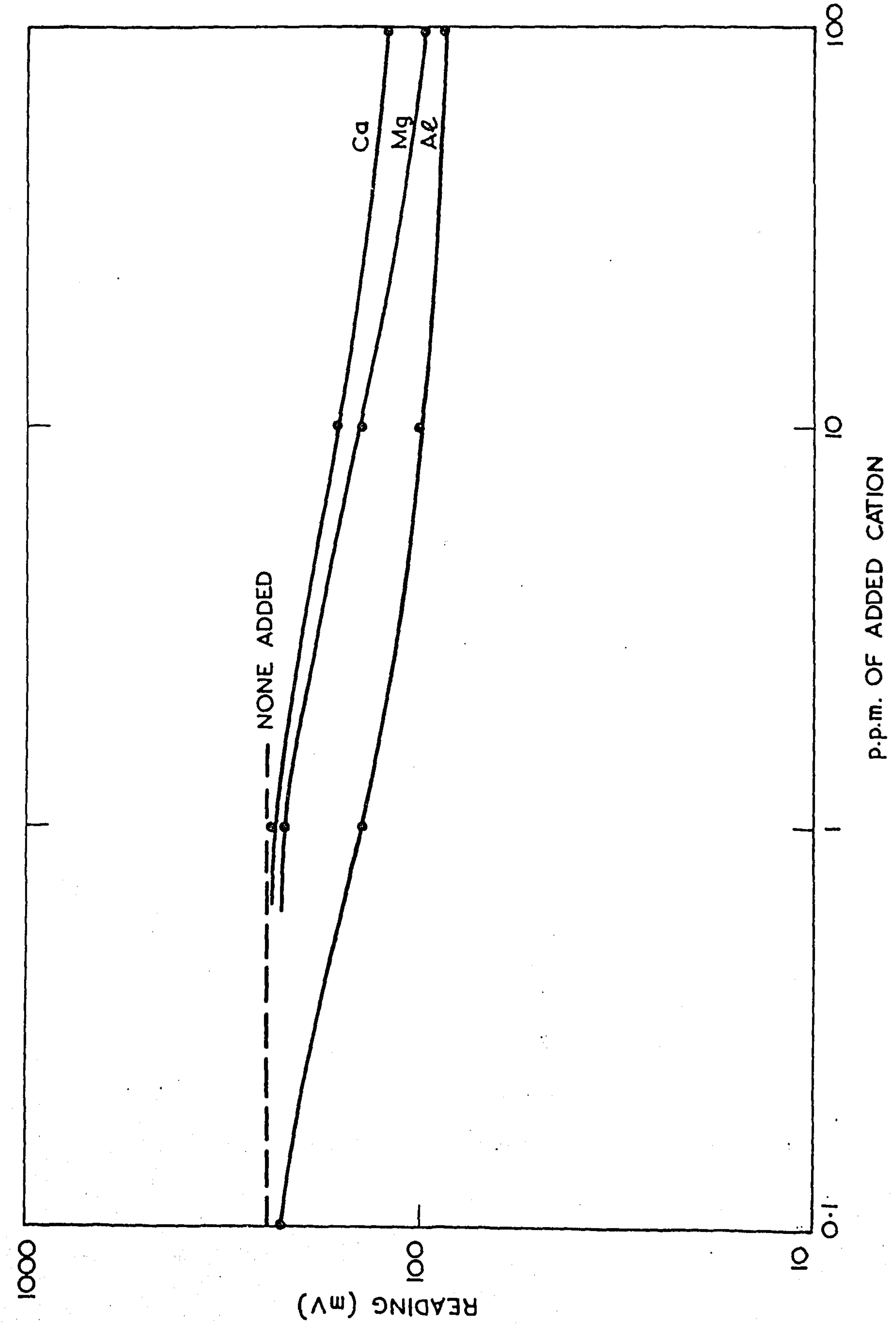

FIGURE 6. CATION INTERFERENCE - Ca. Mg AND Al

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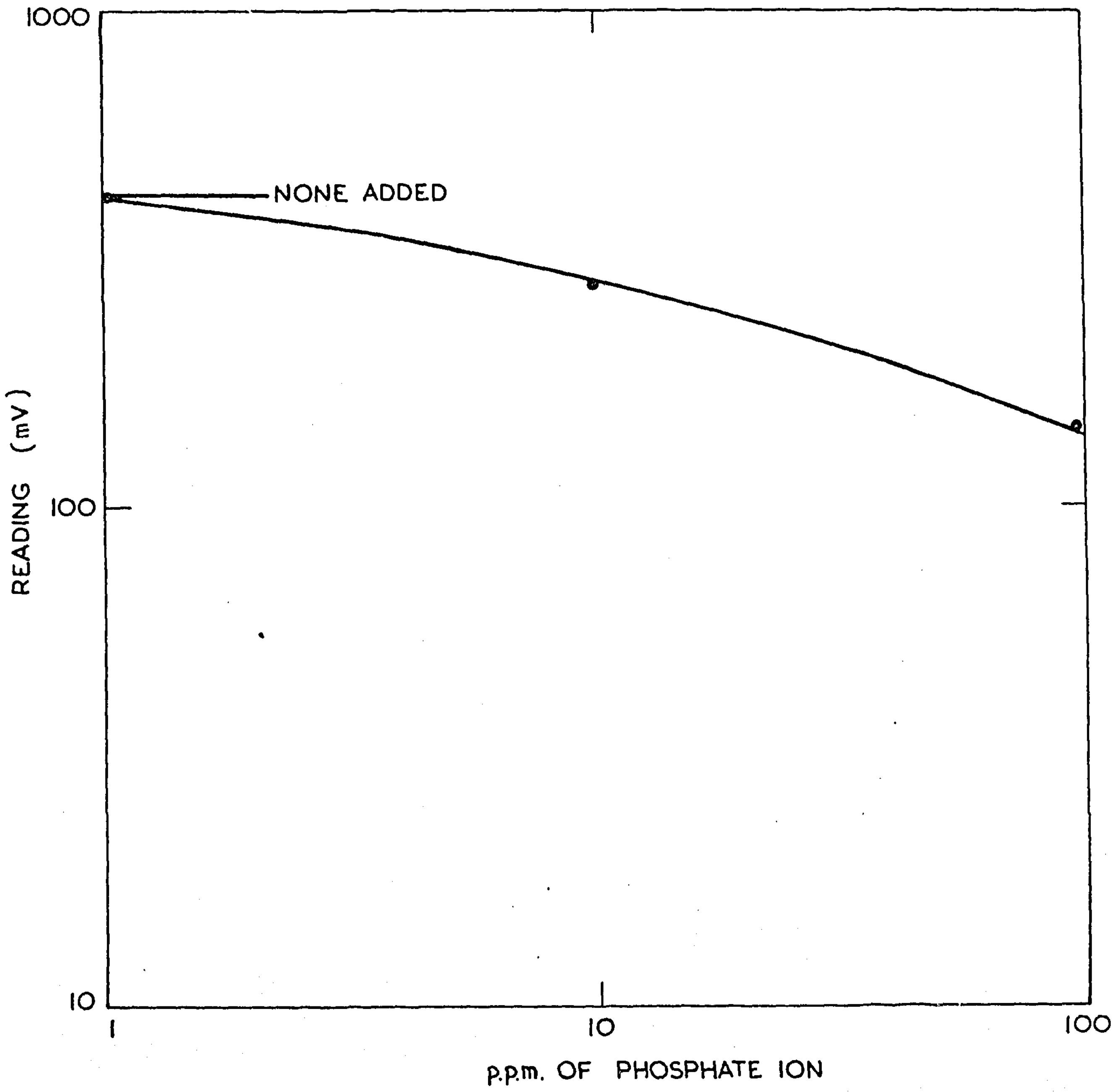

FIGURE 7. EFFECT OF VARYING PHOSPHATE ION CONCENTRATION OF SOLUTION CONTAINING 0.5 p.p.m. Be

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