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ANALYSIS OF SOIL EXTRACT SOLUTIONS BY DIRECT READING EMISSION SPECTROMETRY

by

L.S. DALE
C.E. MATULIS

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ABSTRACT

A rapid spectrometric method was developed for the determination of trace and major elements in aqueous soil extract samples. The rotating disc technique with high voltage excitation was used in conjunction with a direct reading spectrometer.

The procedure determines simultaneously zinc, cobalt, lead, copper, nickel, manganese and vanadium at concentrations of between 1 and 1000 mg ℓ^{-1} together with calcium, magnesium, aluminium and iron at levels usually in excess of 1000 mg ℓ^{-1}. Lutetium is used as an internal standard. The coefficients of variation for all elements range between 2 and 15 per cent.

The following descriptors have been selected from the INIS
Thesaurus to describe the subject content of this report for
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to IAEA-INIS-12 (INIS: Manual for Indexing) and IAEA-INIS-13 (INIS:
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ACCURACY; ALUMINIUM; CALCIUM; COBALT; COPPER; EMISSION SPECTROSCOPY;
INTERFERING ELEMENTS; IRON; LEAD; MAGNESIUM; MANGANESE; MEASURING
METHODS; QUANTITATIVE CHEMICAL ANALYSIS; SOILS; VANADIUM; ZINC

CONTENTS

1.   INTRODUCTION

Rapid determination of trace and major elements in soil extract samples originating from environmental survey programs is often important. Because of the wide variation in concentrations encountered in these samples, a technique is required which has the capability of processing large batches of samples without the need for excessive sample preparation. Atomic absorption spectrometry is used extensively for analysing environmental samples because it provides high sensitivity and is fairly rapid. However it is a single element technique and calibrations are linear only over a limited range of concentration.

Direct reading emission spectrometry is ideally suited to this type of environmental sample. The technique is rapid, has moderate sensitivity, measures all programmed elements simultaneously and it can cover wide concentration ranges when suitable analytical lines are selected. Baer & Hodge [1960] discussed well-established techniques for the direct analysis of solutions. Of these techniques the rotating disc procedure for analysing solutions with high total solids has been used in a variety of applications with both photographic and direct reading emission spectrometers. Applications include the analysis of natural water [Kopp & Kroner 1965], lake waters [Meloche & Shapiro 1954], plant tissue [Chaplin & Dixon 1974; Jones & Weaver 1967] and foodstuffs [Paolini & Kennedy 1962].

To account for variations in exposures and excitation, the addition of an internal standard element is necessary to increase the precision of the procedure. Ionisation interferences frequently occur in high voltage spark excitation [Margoshes 1967] and are due to the varying concentrations of the major components. Interferences of this kind can be effectively stabilised by the addition of a buffer, usually lithium which, when present in excess, swamps the effect of the major components and ensures reproducible ionisation characteristics between samples and standards.

Although buffering has the advantage of suppressing ionisation inter-ferences, it was neither appropriate nor convenient here because the samples were required to be analysed for other anions and cations by respectively wet chemical and atomic absorption methods; the addition of large quantities of buffer could have complicated these analyses. However, the addition of a small quantity of an internal standard element during sample preparation did not significantly alter the composition of the sample.

Ionisation interferences present were overcome by a close matching of analytical to internal standard lines.

Since the most sensitive spectral lines originate from both neutral atoms and ions, it was necessary to choose an internal standard for which both atom and ion lines of adequate sensitivity could be selected. Lutetium was found to be most satisfactory in this respect. Its suitability was verified by assessing the recoveries on spiked samples and also by observing the variation of the analytical line/internal standard line ratios for synthetic samples containing varying amounts of sodium.

Selection of appropriate internal standard lines has made possible the development of a procedure for determining elements in the presence of ionisation interferences without adding a buffer.

2. EXPERIMENTAL

2.1 Apparatus and Spectrometric Operating Conditions

These are given in Table 1.

2.2 Sample Preparation

Soil samples were evaporated to dryness at 110°C and then ashed in a furnace at 410°C. A 20 g sample was digested with 50 mℓ de-ionised water and 5 mℓ 15 M nitric acid at low heat for 30 minutes. It was then cooled and filtered through a Whatman No. 541 filter paper into a 50 mℓ volumetric flask. The residue was washed with small amounts of water and added to the bulk. The flask was made up to volume with de-ionised water after the addition of 0.5 mℓ of 100 g ℓ^{-1} lutetium in 5% nitric acid.

2.3 Analytical Spectral Lines

Table 2 lists the lines used, together with their excitation potentials. Ionisation potentials for the various elements are also given. For the Cu, Zn, Co, Pb, Al and Ni lines, Lu I 4518.6 Å was used as an internal standard and for the V, Mn, Mg and Ca lines, Lu II 2615.4 Å.

2.4 Calibration Standards and Working Curves

Standard solutions of the individual elements were prepared by dissolving either A.R. or Specpure reagents in nitric acid. For some elements, hydrochloric acid was required for dissolution.

Two sets of standard solutions were prepared. The first contained Cu, Mn, Zn, Pb, Co, Ni and V at concentrations of 20, 50, 100, 200, 500 and 1000 mg ℓ^{-1}. The other contained Ca, Mg, Al and Fe at concentrations of 100, 200, 500, 1000, 2000, 5000 and 10 000 mg ℓ^{-1}. In all cases, the final solution contained 5% nitric acid. Each standard contained 1000 mg ℓ^{-1} Lu.

Working curves on log-log coordinates were obtained by plotting concentration against the mean ratio of the net counts (line minus background) to the counts for the internal standard line. Three exposures of each standard

were made. Background measurements were derived from exposures of 5% nitric acid.

2.5 Data Conversion

To speed up processing of the results, two computer programs were written using the ACL-NOVA system [Sanger 1971, 1972]. The first program set up the working curves from calibration data and the second transformed sample ratios to element concentration.

2.6 Investigation of Interferences

To ascertain the reliability of the method, a selection of samples was spiked with known amounts of the various trace elements and recoveries were determined. At this stage of the development of the method, only the Lu II 2615.4 Å line was used as internal standard. Acceptable recoveries were obtained for elements whose lines originated from ions (Mn,V), but substantially higher recoveries were obtained for elements whose atom lines were used (Co, Cu, Pb, Ni).

Zinc showed anomalous behaviour in that the use of the Lu ion internal standard line gave better results than the neutral atom line. The results for Co, Cu, Pb and Ni seemed to suggest that ionisation interferences were responsible for the enhancement of the neutral atom line intensities. Such interferences could arise from ionisation of the major components such as calcium, magnesium and aluminium in the samples. In order to correct for these interferences, the Lu 4518.6 Å line was installed in the spectrometer and used as internal standard for the neutral atom lines. Recoveries for Co, Cu, Pb and Ni in the spiked samples were then acceptable.

It was evident from the observed variations in the excitation index (taken as the ratio of the Lu II to Lu I) that ionisation interferences were responsible for the observed enhancement of neutral atom lines. Since the interference also occurred on the Lu I line, the ratio was adequately corrected. The adequacy of this correction is verified by the comparison of results as shown in Tables 3 and 4.

With the interference now identified, the extent to which the internal standard corrected for extreme variations in interference still had to be determined. To accomplish this, synthetic solutions were prepared containing copper and manganese in the presence of 1000 mg ℓ^{-1} lutetium and varying concentrations of sodium. Sodium was chosen since it has a fairly low ionisation potential and is therefore a plentiful source of ions using high voltage excitation. Table 5 shows the variation of the line pair ratios for copper and manganese. The Cu I 3247.6 Å and Mn II 2933.1 Å were chosen

as typical neutral atom and ion lines respectively. The sodium concentration was varied between 0 and 45 000 mg ℓ^{-1}. The results indicate, within the limits of the experimental error, the extent to which the appropriate internal standard lines can cope with large variations in concentration of interferent. These variations are considered to be far in excess of those encountered in real samples.

2.7 Detection Limits

Detection limits for the trace elements are shown in Table 6. These are based on twice the standard deviation of the blank reading, using the conditions described. These conditions were found to give the best signal-to-background ratios for the lines considered. Changes in source parameters, such as inductance and capacitance, showed no significant improvement in signal-to-background ratio.

The detection limits quoted do not necessarily represent the optimum. There are several reasons for this; the most sensitive lines of all the elements were not used in all cases because of space limitations on the focal plane of the spectrometer. The detection limit is also dependent on the sensitivity and dark current of the photomultiplier.

2.8 Precision

The precision was assessed from replicate exposures of standards, the standard deviation of the mean line pair ratios ranged between 2 and 15 per cent (Table 7).

3. DISCUSSION

The rotating disc technique with high voltage spark excitation used in conjunction with a direct reading spectrometer enables a range of elements to be determined simultaneously in solutions containing high total solids. In soil extract samples, where concentrations of trace and major constituents can vary over wide ranges, this technique has a number of advantages. First, calibrations are linear over wide concentration range; in the procedure described, the range of linearity is 10 to 1000 mg ℓ^{-1}. (An exception is the calibration for copper which shows curvature towards the higher concentrations); this linearity eliminates the need for dilution when high levels of elements are encountered. A second, lies in the determination of calcium and magnesium in the presence of aluminium. With this technique no suppression effects are observed, whereas in atomic absorption spectrometry both calcium and magnesium are subject to chemical interference from aluminium. A releasing agent such as lanthanum is added to remove this interference and this step renders the analyses very time-consuming.

A major problem associated with soil extract samples is the matrix effect arising from the presence of varying amounts of major constituents. This work has shown that ionisation interferences can cause marked changes in the line pair ratio unless suitable internal standard lines are used. Selection of appropriate internal lines eliminates the need to add buffers and simplifies sample processing. The use of both neutral atom and ion lines as internal standards also permits the degree of interference encountered in samples to be assessed by observing the excitation index. The suitability of the internal standard lines used is verified by the agreement obtained for the spiked samples and samples which had been analysed by other methods.

Another type of interference which can occur, particularly in direct reading spectrometry, is that arising from near-coincident lines because of the major constituents. This was investigated and, apart from iron at concentrations greater than those normally encountered in these samples, no such interferences were observed.

The detection limits obtained are affected by a number of parameters. Limitations on space on the focal plane of the spectrometer and on the size of exit slits and photomultiplier tubes prevent the most sensitive line being used in some cases. The need to use second order lines as a result of these limitations also affects the detection limit.

The most important aspect is the background since, by definition, the detection limit is dependent on the magnitude and variability of the background. Stability of the background continuum depends largely on the variations in exposures, the fluctuation of the dark current level, and the sensitivity of the photomultiplier tubes. Therefore tubes must be selected with low dark current, high stability and high sensitivity for optimum performance. High dark current photomultiplier tubes must be avoided if relatively small background readings, which are of the same magnitude as the dark current, are encountered. The photomultiplier tubes used were those normally supplied by the manufacturer but only those with low dark currents were used.

A further consideration in optimising detection limits is the choice of those electrical source parameters such as inductance and capacitance which give the best signal-to-background ratios. These were investigated extensively and the parameters chosen represent the conditions yielding maximum ratios.

4. CONCLUSIONS

The procedure described has been found suitable for the simultaneous determination of trace and major elements in soil extract solutions. By incorporating appropriate internal standard lines, ionisation interferences are minimised and the need for buffering eliminated. The advantages of this technique include the speed of analysis, the linearity of calibration, the multi-element capability and the high sample throughput.

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TABLE 1

APPARATUS AND SPECTROMETRIC OPERATING CONDITIONS

Spectrometer	1.5 m Compact Atomcounter Model 66-000 (Jarrell-Ash Co.)
Grating	Concave, 1180 grooves mm^{-1}, blazed at 3600 Å
Wavelength Range	2000-8000 Å
Reciprocal Linear Dispersion	5.6 Å mm^{-1}
Entrance Slit	25 μm
Exit Slits	75 μm
Excitation Source	high voltage spark (Jarrell-Ash Varisource)
Capacitance	0.005 μFd
Inductance	150 μH
Breaks per half cycle	4
RF Current	3.6 A r.m.s.
Electrodes	disc electrode; 3mm wide, 12 mm dia. (similar to ASTM D-1), Ringsdorff RW 1576, mounted in rotating disc assembly, motor speed 8 rev m^{-1} counter electrodes, ASTM C-5 fabricated from National L3809 AGKSP rod.
Sample Containment	Porcelain combustion boats, 2 mℓ capacity.
Analytical Gap	3 mm
Preburn	10 s
Exposure	30 s
Photomultipliers	RCA 1P28, selected for low dark current, Corex refractor plates used for slits in second order.

TABLE 2

ANALYTICAL SPECTRAL LINES, EXCITATION POTENTIALS
AND IONISATION POTENTIALS*

Element	Wavelength (Å)		Order	Excitation Potential (eV)	Ionisation Potential (eV)
Zn	I	3345.6	2	7.78	9.391
Co	I	3405.1	1	4.07	7.86
Pb	I	4057.8	1	4.37	7.415
Cu	I	3247.6	2	3.82	7.724
Ni	I	3414.8	2	3.65	7.633
Al	I	3944.0	2	3.14	5.984
Mn	II	2933.1	1	5.40	7.432
V	II	3110.7	1	4.33	6.74
Mg	II	2795.5	1	4.43	7.644
Ca	II	3158.9	2	7.05	6.111
Fe	II	2599.4	2	4.77	7.87
Lu	II	2615.4	1	4.74	6.15
Lu	I	4518.6	1	2.74	6.15

* Excitation potentials and ionisation potentials from
   Meggers, Corliss and Scribner (1961)

TABLE 3

A COMPARISON OF RESULTS OBTAINED ON SPIKED SAMPLES

Sample No.	Element	Concentration Added (mg ℓ^{-1})	Concentration Found (mg ℓ^{-1})
704-1	Pb	16	13
704-2	Pb	39	40
702-2	Pb	102	73
702-1	Cu	22	24
705-1	V	20	22
705-2	V	38	43
705-3	V	99	110
702-1	Mn	245	230
702-2	Mn	144	130
702-3	Mn	81	60
702-4	Mn	41	40
702-1	Ni	42	57
702-2	Ni	104	115
702-3	Ni	211	185
703-1	Zn	204	175
704-1	Co	108	115
704-2	Co	43	54
702-2	Co	266	245

TABLE 4

A COMPARISON OF RESULTS OBTAINED ON CHEMICALLY ANALYSED SAMPLES*

Element	Concentration Present (mg ℓ^{-1})	Concentration Found (mg ℓ^{-1})
Al	7 000	7 900
Al	10 700	10 200
Ca	136	144
Ca	364	344
Ca	2 360	2 740

* Original Ca contents measured by X-ray fluorescence;
original Al contents by wet chemical method (Pakalns 1965).

TABLE 5

VARIATION OF LINE PAIR RATIO WITH CHANGES

IN SODIUM CONCENTRATION*

Concentration# Na added (mg ℓ^{-1})	$\dfrac{Cu\ I}{Lu\ II}$	C.V. +(%)	$\dfrac{Cu\ I}{Lu\ I}$	C.V. (%)	$\dfrac{Mn\ II}{Lu\ II}$	C.V. (%)	$\dfrac{Mn\ II}{Lu\ I}$	C.V. (%)	Excitation Index Lu II/Lu I	C.V. (%)
0	0.79 ± 0.05	6.0	2.08 ± 0.14	6.7	0.51 ± 0.01	2.9	1.51 ± 0.05	3.1	1.59 ± 0.03	1.9
100	0.84 ± 0.01	1.5	2.31 ± 0.12	5.3	0.66 ± 0.04	6.3	1.43 ± 0.28	19.9	1.51 ± 0.07	4.6
1 000	1.26 ± 0.04	3.4	1.99 ± 0.09	4.3	1.01 ± 0.06	5.5	1.44 ± 0.23	16.0	1.14 ± 0.04	3.5
5 000	1.86 ± 0.06	2.9	2.03 ± 0.29	9.5	0.88 ± 0.09	10.5	1.06 ± 0.22	21.0	0.79 ± 0.05	6.3
10 000	1.79 ± 0.16	8.8	1.21 ± 0.25	20.5	0.76 ± 0.03	4.6	0.55 ± 0.07	12.3	0.59 ± 0.02	3.4
45 000	2.02 ± 0.11	5.4	0.90 ± 0.01	1.2	0.60 ± 0.01	1.8	0.30 ± 0.04	13.7	0.42 ± 0.02	4.8

* Lines used are Cu I 3247.6 Å, Mn II 2933.1 Å, Lu I 4516.8 Å, Lu II 2615.4 Å

\# All in 5% HNO_3 acid. Excitation index based on 8 values.

+ Coefficient of Variation = $\dfrac{\sigma}{x} \cdot \dfrac{100}{\sqrt{n}}$, limits quoted for all line ratios are 1σ for 4 values   n = number of determinations.

TABLE 6

DETECTION LIMITS FOR TRACE ELEMENTS

Element	Detection Limit (mg ℓ^{-1})
Zn	10
Mn	2
V	3
Ni	20
Pb	10
Cu	0.2
Co	5

TABLE 7

PRECISION DATA FOR ANALYTICAL LINE-INTERNAL STANDARD LINE RATIO

Analytical Line/Internal Standard Line Ratio	Concentration Level (mg ℓ^{-1})	Coefficient of Variation of the Mean (%)
Zn/Lu I	50	1.8
Co/Lu I	50	14.7
Pb/Lu I	50	12.8
Ni/Lu I	50	6.5
Cu/Lu I	200	6.7
V/Lu II	100	7.8
Mg/Lu II	100	2.4
Ca/Lu II	40	11.3
Al/Lu II	1 000	2.3
Fe/Lu II	1 000	3.2
Mn/Lu II	200	2.9