

## Use of inductively coupled plasma atomic emission spectrometry for determination of iron, aluminium and phosphorus in Tamm's soil extracts

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### **Abstract**

Iron, aluminium and phosphorus were determined by ICP atomic emission spectrometry in an ammonium oxalate-oxalic acid extract of soil. Measuring conditions were optimized towards phosphorus. Transport interferences were prevented by diluting and acidifying the sample solutions. Spectral interferences on phosphorus were found with Fe, Al and Cu.

A correction may be made for soils high in Al and/or Fe. The analytical results for all three elements Fe, Al and P showed good agreement with other methods of determination.

### **Introduction**

An acid ammonium oxalate solution, which contains  $(\text{COONH}_4)_2$  at 0.175 mol/l and  $(\text{COOH})_2$  at 0.100 mol/l and has a pH value of 3.25, is commonly known as Tamm's reagent (Tamm, 1934). Several modifications have been proposed, for example 0.113 mol/l  $(\text{COONH}_4)_2$  and 0.087 mol/l  $(\text{COOH})_2$  with pH 3.0 (Schwertmann, 1964). These solutions are recognized as selective extraction agents for the active colloidal fraction of iron and aluminium in soils, provided that the extraction is carried out in the dark. This extraction was also found to be very useful for assessing the phosphate retention characteristics of soils (Schlichting, 1962; Saunders, 1965; Beek, 1980). For this purpose, the phosphate concentration in the extract has to be measured as well as the aluminium and iron concentration. The latter two can be determined rapidly by flame atomic absorption spectrometry (FAAS) (Blakemore, 1968), but for the determination of phosphorus – by means of the molybdenum blue method (Murphy & Riley, 1962) – the extract has to be digested, a procedure which substantially slows down the rate of analysis. This calls for an analytical

technique with multi-element capability and without pre-digestion. Both requirements are met by the technique of inductively coupled plasma atomic emission spectrometry (ICP-AES).

Moreover, this technique has high sensitivity and relative freedom from chemical interferences. The plasma conditions are suitable for the excitation and measurement of non-metals such as phosphorus too. Notwithstanding these advantages, spectral and matrix interference effects are a potential source of error. This paper reports the (virtually simultaneous) determination of aluminium, iron and phosphorus in oxalate extracts of soils by means of ICP-AES. Actual and potential inter-element interferences in the plasma are discussed together with procedures to overcome these interferences.

## Materials and methods

### *Instrumentation*

The apparatus used in this investigation was a commercially available Perkin-Elmer ICP/5500, equipped with a holographic UV grating of 2880 grooves per mm, blazed at 210 nm, focal length 408 mm, resulting in a spectral band width of 0.03 nm. The ICP unit is crystal-controlled at 27.12 MHz; intensity measurements at preselected wavelengths are taken sequentially. The read-out system is interfaced with an 8-bit 64 kByte micro-computer with a dual floppy disc unit, a video screen and a printer. Gross line intensities were measured at 214.91 nm (P I), 396.15 nm (Al I) and 238.20 nm (Fe II). Background intensities were obtained by measuring blank solutions. Operating parameters (Table 1) were optimized for the phosphorus line.

### *Sample preparation for ICP-AES*

Sandy soils with a low P content and a high Cu content were available from another investigation. Twenty of those were chosen at random.

From several slightly different extraction procedures, the one used by Beek (1980) was adopted. In this procedure 2.50 g of air-dry soil (particle size < 2 mm) is extracted by 50 ml of a solution which contains ammonium oxalate at 0.200 mol/l and oxalic acid at 0.140 mol/l. The extraction time was 120 min at 120 oscillations/min on a linear, mechanical shaker in a darkened room at  $20 \pm 1$  °C. Thereafter the suspensions were filtered over paper. An aliquot of each filtrate was

Table 1. Operating parameters.

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|   |
|---|
| Incident power 1.25 kW                                  |
| Reflected power <5 W                                    |
| Intermediate gas flow rate 0.70 l/min                   |
| Outer gas flow rate 14 l/min                            |
| Sample carrier gas flow rate 0.55 l/min                 |
| Observation height 13 mm above the top of the load coil |
| Integration time 2 s                                    |
| Number of replicates 3                                  |

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acidified with HCl and diluted tenfold so as to obtain a final solution containing HCl at 0.1 mol/l.

Conventional nebulizers (the pneumatic cross-flow type) can only operate efficiently if aspirated solutions contain less than 0.5 % total dissolved solids. Since the extracts contained some 37.4 g l<sup>-1</sup> of oxalates, dilution was necessary. A dilution factor of 10 had to be applied so as to achieve consistent results. Furthermore, in order to increase the solubility of the oxalates present and to prevent the build-up of solids in the central torch tube, all solutions were acidified with HCl up to a concentration of 0.1 mol/l. The reproducibility was increased by addition of glycerol to all solutions to an extent of 1 % (v/v) (van Eck, 1978).

### *Measurements*

Each solution was analysed for P, Al and Fe by ICP-AES. For the calibration, series of mixed standard solutions were prepared which contained up to 10 mg l<sup>-1</sup> of P, Al and Fe, and had the same concentrations of oxalate, HCl and glycerol as the diluted soil extracts. The ICP measurements were done in triplicate, i.e. three readings of the same measuring solution were taken with intervals of 10-15 seconds while the solution was nebulized continuously. For comparison, the concentrations of Al and Fe in the filtrates were determined by FAAS, with a C<sub>2</sub>H<sub>2</sub>/N<sub>2</sub>O flame at 309.3 nm and a C<sub>2</sub>H<sub>2</sub>/air flame at 248.3 nm, respectively. The phosphate concentration was measured in a separate aliquot by the molybdenum blue method after preceding digestion of the extract by concentrated H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>. These determinations were carried out independent of ICP determinations, i.e. on a different subsample, by another operator at another time.

## **Results and discussion**

### *Spectral interferences*

Solutions containing 10 mg l<sup>-1</sup> of P, Al and Fe were aspirated for spectral calibration of the analytical wavelengths and for calibration of the sensitivity ('gain'). Then solutions containing 1000 mg l<sup>-1</sup> of Al, Ca, Cu, Fe, K, Mg, Mn, Na, P and Ti were nebulized into the plasma, and the apparent concentrations of phosphorus, aluminium and iron were measured at the relevant analytical wavelength to check for any spectral emission originating from elements other than the analyte.

At these conditions it was found that K, Mg, Mn, Na and Ti did not cause interferences at the lines chosen for P, Al and Fe. At the same conditions, however, spectral interferences were observed for Ca on Al, Al on P, Fe on P and Cu on P.

The interference of Ca on Al could be compensated by background correction at low Ca concentrations. In practice, the Ca levels are low because of the poor solubility of calcium oxalate. To suppress any residual influence, background correction was applied on both sides of the Al line at distances of 0.10 nm.

The spectral interference of Al on P is brought about by two phenomena: a broad-band continuum and an emission line at 215.05 nm (Fig. 1). In this situation background correction facilities at our instrument lead to overcompensation at higher Al levels. From Table 2 it follows that the overlap gives rise to an apparent P

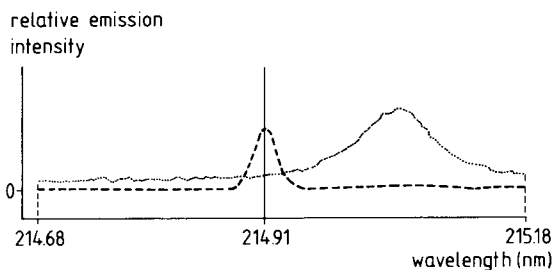


Fig. 1. Emission spectrum of Al and P. Scan over 0.5 nm around 214.91 nm (P I). ---- P 10 mg l<sup>-1</sup>; .... Al 250 mg l<sup>-1</sup>.

concentration of 1 mg l<sup>-1</sup> at an Al level of 155 mg l<sup>-1</sup>. This means that 10 mg l<sup>-1</sup> Al used as the highest standard gives an apparent P concentration of 0.07 mg l<sup>-1</sup> ( $\equiv$  0.43 mmol P per kg soil). In soil extracts without any Al present this would mean that the measured P value is 0.43 mmol kg<sup>-1</sup> too low. Actually, some Al is always present in soil extracts which tends to compensate for this error so that no special corrections are necessary. At Al concentrations falling beyond the standard series, however, on-line correction should be considered.

The interference of Fe on P is illustrated in Fig. 2. The overlap gives rise to an apparent P concentration of 1 mg l<sup>-1</sup> at a Fe level of about 930 mg l<sup>-1</sup> (Table 2). Following the same reasoning as above, it can be inferred that an apparent P concentration of about 0.01 mg l<sup>-1</sup> ( $\approx$  0.06 mmol P per kg soil) would be caused by extractable Fe at a level of about 10 mg l<sup>-1</sup>. Hence, at Fe concentrations falling within the standard series negligible errors are made. As in the case of Al, on-line correction is possible, but this would only be necessary at extremely high levels of extractable Fe in soils.

A very serious spectral interference in the determination of P at 214.91 nm is caused by the copper emission line at 214.90 nm. Aspiration of Cu at 1 mg l<sup>-1</sup> gave a signal equal to P at 0.65 mg l<sup>-1</sup>. Furthermore, the peak search routine in the P-E instrument is designed in such a way that it cannot distinguish between two overlap-

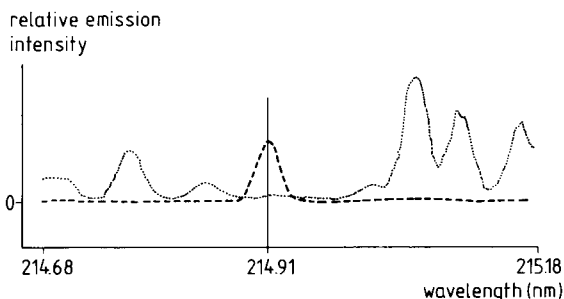


Fig. 2. Emission spectrum of Fe and P. Scan over 0.5 nm around 214.91 nm (P I). ---- P 10 mg l<sup>-1</sup>; Fe 1000 mg l<sup>-1</sup>.

Table 2. Spectral interference from Fe and Al at the P I emission line at 214.91 nm.

| Solution composition     |                          | IEC*                  |
|--------------------------|--------------------------|-----------------------|
| Fe (mg l <sup>-1</sup> ) | Al (mg l <sup>-1</sup> ) | (mg l <sup>-1</sup> ) |
| 250                      | 0                        | 0.28                  |
| 500                      | 0                        | 0.54                  |
| 1000                     | 0                        | 1.03                  |
| 0                        | 250                      | 1.60                  |
| 0                        | 500                      | 3.23                  |
| 0                        | 1000                     | 6.44                  |
| 100                      | 500                      | 3.35                  |
| 250                      | 250                      | 1.84                  |
| 500                      | 100                      | 1.16                  |
| 500                      | 500                      | 3.67                  |

\* Interferent Equivalent Concentration (IEC) is the apparent analyte concentration caused by interfering concomitants measured at a certain level of analyte without background correction:

$$\text{IEC} = \frac{\text{intensity concomitants}}{\text{intensity analyte}} \times \text{concentration analyte.}$$

ping peaks, but looks for the top within a certain wavelength interval ( $\pm 0.015$  nm) around the supposed position. This means, that the gross emission signal from solutions containing both Cu and P does not only depend on the actual concentrations of interferent and analyte, but also on the ratio of these concentrations. Fortunately, the solubility of copper (II) oxalate is low. At the extraction conditions used here (pH 3, oxalate 0.34 mol/l) the expected Cu concentration in the tenfold diluted extract is estimated to be at most 0.17 mg l<sup>-1</sup>. Moreover, the total copper content of soils is usually not high enough to reach even that value (Bowen, 1979). Indeed, ICP measurements of the present oxalate extracts at another Cu line (324.75 nm) resulted in zero values. It is obvious that Cu interferences may be present when extraction solutions with low pH and/or low oxalate concentrations are used. In such situations the use of a P line in vacuum UV may be considered.

It follows from the above discussion that all samples which gave emission values within the calibration range need not be corrected for spectral interference from Al or Fe. In case of too high Al or Fe content, the extract should be diluted further; the value originally found for the P concentration should then be corrected for the influence of Al and/or Fe.

### *Analytical performance*

The results of analysis of soil extracts are given in Table 3.

The results for the P determination show a good agreement between ICP-AES and the molybdenum blue method in the investigated range of 2-35 mmol kg<sup>-1</sup> (Table 4).

For the Al determination also a good correlation was found between ICP-AES and FAAS. In the investigated range of 5-85 mmol kg<sup>-1</sup> the difference was never

Table 3. Analytical results for Al, Fe and P measured by ICP-AES and reference methods in non-calcareous sandy soils (mmol kg<sup>-1</sup> of air-dry soil).

| Soil number | Al   |      | Fe   |      | P                  |      |
|-------------|------|------|------|------|--------------------|------|
|             | AAS  | ICP  | AAS  | ICP  | spectrophotometric | ICP  |
| 1           | 42.6 | 44.9 | 16.0 | 14.4 | 19.7               | 19.9 |
| 2           | 51.6 | 52.7 | 16.6 | 14.7 | 20.7               | 20.7 |
| 3           | 14.6 | 17.2 | 37.5 | 35.1 | 9.5                | 9.5  |
| 4           | 71.8 | 70.4 | 12.4 | 11.4 | 10.2               | 10.1 |
| 5           | 66.1 | 68.0 | 28.1 | 24.6 | 0.2                | <2   |
| 6           | 56.0 | 57.4 | 5.1  | 4.1  | 1.4                | <2   |
| 7           | 47.1 | 47.9 | 46.5 | 45.6 | 34.5               | 34.7 |
| 8           | 49.3 | 48.5 | 49.1 | 44.8 | 34.9               | 35.4 |
| 9           | 65.3 | 64.7 | 11.5 | 10.1 | 6.7                | 6.0  |
| 10          | 33.8 | 32.3 | 7.3  | 6.2  | 9.6                | 7.9  |
| 11          | 84.4 | 84.8 | 21.4 | 17.8 | 0.8                | <2   |
| 12          | 69.2 | 69.7 | 6.1  | 5.3  | 0.6                | <2   |
| 13          | 72.0 | 68.1 | 4.0  | 3.9  | 1.4                | <2   |
| 14          | 55.9 | 57.3 | 28.7 | 27.5 | 0.4                | <2   |
| 15          | 55.0 | 59.2 | 24.0 | 22.5 | 7.9                | 7.2  |
| 16          | 22.8 | 26.2 | 8.3  | 7.1  | <0.1               | <2   |
| 17          | 55.4 | 56.5 | —    | 11.3 | 10.1               | 9.4  |
| 18          | 50.9 | 52.7 | 44.8 | 44.5 | 6.6                | 5.5  |
| 19          | 56.3 | 54.0 | 46.9 | 45.6 | 13.6               | 12.0 |
| 20          | 7.2  | 5.5  | 22.8 | 21.3 | 1.2                | <2   |

greater than 4 mmol kg<sup>-1</sup>, which is quite acceptable for the higher levels.

The values for Fe found by ICP-AES are consistently lower than those found by FAAS, on an average 2 mmol kg<sup>-1</sup> in the investigated range of 4-45 mmol kg<sup>-1</sup>. It is not clear whether the ICP values are too low or the AAS values are too high. Apart from this systematic difference, however, the regression parameters show good correlation.

The sensitivity of the ICP compared with the reference methods used here is much higher in the case of Fe and Al, while for P the sensitivity of ICP is limited. Winge et al. (1979) report for the P line used a detection limit of 0.076 mg l<sup>-1</sup>.

In Fig. 3 is shown that the above described method for P in routine analytical practice can be used down to 0.3 mg l<sup>-1</sup> which corresponds with 2 mmol P per kg

Table 4. Linear regression parameters for ICP determination of P, Al and Fe with regard to the reference methods.

| Parameter               | P      | Al     | Fe     |
|-------------------------|--------|--------|--------|
| Slope                   | 1.046  | 0.978  | 0.975  |
| Intercept               | -1.18  | 1.7    | -1.0   |
| Correlation coefficient | 0.9986 | 0.9947 | 0.9976 |
| Number of observations  | 12     | 20     | 19     |

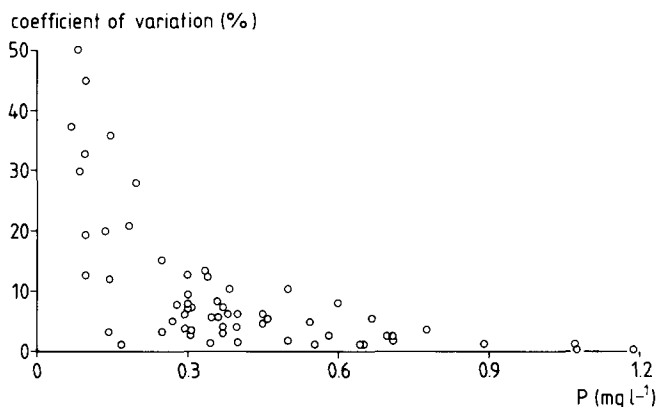


Fig. 3. Coefficient of variation of ICP-AES measurements as a function of P concentration.

soil. At higher levels coefficients of variation of the measurements lie between 1 to 2 %.

The use of ICP-AES for these determinations offers the advantage of speed, since all three elements are measured almost simultaneously in one and the same extract, without further preparations except for a simple filtration and dilution. Because of the absence of serious interferences of the method, it is reasonable to assume that the usefulness is not limited to the sandy soils of the present study: the method may be applied to other soil types as well.

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