

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF JYVÄSKYLÄ
RESEARCH REPORT No. 60

**DEVELOPMENT OF METHODS FOR FERTILIZER ANALYSIS BY INDUCTIVELY
COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY**

BY
ROSE MATILAINEN

Academic Dissertation
for the Degree of
Doctor of Philosophy



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and Natural Sciences of the University of Jyväskylä, for public examination
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- II Matilainen, R., & Tummavuori, J., Determination of Magnesium in Fertilizers by Inductively Coupled Plasma Atomic Emission Spectrometry: Studies of Some Spectral and Inter-element Effects at Different Wavelengths. (1995) *J. AOAC Int.* **78**, 1134-1140.
- III Matilainen, R., & Tummavuori, J., Iron Determination in Fertilizers by Inductively Coupled Plasma Atomic Emission Spectrometry: Study of Spectral and Inter-element Effects at Different Wavelengths. (1996) *J. AOAC Int.* **79**, 22-28.
- IV Matilainen, R., & Tummavuori, J., Determination of Sulfur in Fertilizers by Inductively Coupled Plasma-Atomic Emission Spectrometry: Spectral and Inter-element Effects at Various Wavelengths. (1996) *J. AOAC Int.* **79**, 1026-1035.
- V Matilainen, R., & Tummavuori, J., Determination of Calcium in Certain Fertilizers by Inductively Coupled Plasma Atomic Emission Spectrometry: Studies of Some Spectral and Inter-element Effects at Different Wavelengths. (1997) *J. AOAC Int.* **80**, 294-297.

PREFACE

This research was carried out in the Department of Chemistry, University of Jyväskylä during the years 1993-1996. The collaborative measurements performed during the years 1991-1993 relate to the research done for my Ph.Lic. degree completed in 1993.

I wish express my profound gratitude to my supervisor, Associate Professor Jouni Tummavuori for his patient and continuous encouragement and support throughout this project. To him I owe my acquaintance with analytical methods and statistical treatments of measurement data; for this valuable opportunity I am very grateful.

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I am also grateful to Michael Freeman for revising the language.

Last but not least, I wish to express my deepest gratitude to my parents, sisters and brothers and their families for their support and understanding during throughout my studies. Not to forget my friends in our sports team, who tolerated my occasional absent-mindedness.

Jyväskylä, May 1997

Rose Matilainen

I dedicate this study to my Parents.

ABSTRACT

Developing the ICP-AES method to a standard method of determination was performed for five nutrients (B, Mg, Fe, S and Ca) in commercial fertilizers. The procedure included finding the best analytical wavelengths on the basis of calibration and interference studies and testing the sample preparation and measurement procedures in collaborative studies. The collaborative studies were done for the determination of water-soluble B, Mg and S and acid-soluble B, Mg, S and Fe by ICP-AES and the accuracy of the method used was in the range 3,7-12% independent of the measurement wavelength used.

To find the best wavelengths for determining of the above-mentioned elements, the calibration lines at three or four wavelengths of each element were analyzed for linearity, detection limits and quantification limits. The regression of the calibration line should be >0.9998 , at which point the limits of detection and quantification will be low enough. Interference studies were done at those wavelengths to find the interference-free determination wavelength. The most important aspect of the interference studies was the mathematically independent combination of the matrix elements (seven potential interfering elements at five concentration levels). Analyzing this subset for the selected element, it is possible to evaluate the interferences of the different matrix elements on the examined element. Multiple linear regression proved a valuable technique in achieving this and it was able to be used because calibration was confined to within a linear range. The observed interferences may be regarded either as an interelement effect or as a spectral effect. The effect is considered a spectral effect when the wavelength of the interfering element is within ± 0.2 nm of the analyte line; if not, the effect is considered an interelement effect. Typically the interelement effects were caused by easily ionizable elements (Ca, K, Na and Mg) and the spectral effects by P, S, B and Fe. The observed interferences agreed in great measure with earlier known interferences, although many new interferences were also found. The best wavelengths according to the calibration and the interference studies were 208.959 nm for B, 383.826 nm for Mg, 238.204 nm for Fe, 180.731 nm for S and 396.847 nm for Ca.

The outlines of the SFS-standards for the determination of water-soluble boron and magnesium and acid-soluble magnesium have already been accepted as new SFS standards by the Chemical Industry Federation of Finland.

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ABBREVIATIONS

a	= Intercept of the calibration line on the y-axis
AS	= Acid-soluble
b	= Slope of the calibration line
dc-APES	= Direct current argon plasma emission spectroscopy
EIE	= Easily ionizable element
ICP-AES	= Inductively coupled plasma atomic emission spectroscopy
LOD	= Limit of detection
LOQ	= Limit of quantification
n	= Number of calibration points or number of samples
r	= Product moment correlation coefficient
s_a	= Standard deviation of the intercept
s_b	= Standard deviation of the slope
s_B	= Standard deviation of the blank measurements
s_d	= Standard deviation in general
t_α	= t-distribution value for chosen confidence level α
WS	= Water-soluble
wt	= Weight
x	= Content of the standard or the sample
x_L	= Limit of detection expressed as concentration
y	= Instrument signal from the standard or the sample
Δy	= Confidence band around a signal obtained from a measurement
\hat{y}	= Fitted y-value on the calculated regression line corresponding to the individual x-values
y_B	= Blank measurement
\bar{y}_B	= The mean of the blank measurements
y_L	= The smallest discernible analytical signal
ν	= Degrees of freedom

1. INTRODUCTION

The aim of this study was to develop new standard methods for the determination of certain fertilizer elements by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Developing a standard method of determination includes finding the analytical wavelengths which best satisfy demands both as to the linearity of calibration at the selected ranges and interference-free determination, finding suitable sample digestion methods, testing the method in collaborative studies and, finally drawing analytical conclusions on the basis of the statistical methods used.

ICP-AES is a relatively new analytical method the use of which in fertilizer analysis began at the turn of the 1980s. However, its use in fertilizer analysis is not standardized and it has not been adopted by the AOAC as one of the official final action methods. In the analytical literature there are only a few reports on the determination of fertilizer elements, especially trace and minor elements, by argon plasma methods (direct current argon plasma dc-APES,¹⁻³ inductively coupled argon plasma ICP-AES⁴⁻⁷). According to these reports, the method has proved sufficiently sensitive, rapid and generally capable of determining elements in solutions over several concentration levels with minimal matrix effects.⁴⁻⁷

To find the best analytical wavelengths for each of the fertilizer elements analyzed, the calibration procedure and interference of the fertilizer matrix elements at these wavelengths were critically examined. For each element the three or four most used analytical wavelengths were selected. In calibration procedure attention is paid to linearity as well as to the limit of detection and limit of quantification. In interference studies the effects of the combined fertilizer matrix elements on the element analyzed were calculated at selected wavelengths using multiple linear regression procedure. Multiple linear regression analysis can be used in calculating the effects of matrix elements because calibration is confined to the linear range.

In earlier interference studies by other authors each potentially interfering element was isolated and examined separately. One must remember that the potentially interfering element are present all together in the real sample solutions to be analyzed. By analyzing the effects of combined matrix elements, it is possible to calculate their total effects without isolating

them separately. Single element studies do not necessarily yield correct observations, because the combined effects of the interfering elements may strengthen, weaken or compensate for each other's emission intensities.

In dissolving the fertilizer samples both water-soluble (WS) and acid-soluble (AS) methods were used, as is already the case with other techniques, and were either wholly or in part included among the AOAC official final action methods.⁸ It was found that these sample solution preparation methods are directly applicable to ICP-AES analysis, and hence collaborative determination studies were done for certain fertilizer elements. Measurements were done in four independent ICP-AES laboratories on two commercial fertilizers: NPK 20-4-8 and NPK 25-4-4. In their measurements each laboratory used their own optimized ICP-AES instrument at the ordinarily used analytical wavelength. The preparation of fertilizer sample solutions and calibration standard solutions were done according to instructions from the ICP-AES working group of the Chemical Industry Federation of Finland. Each element was determined in three groups, and each group included six sub-samples. Hence for one element from one fertilizer with one digestion method 18 separate samples and measurements were done. Thus the total number of measurements of an element using one digestion method from one fertilizer were $4 \times 3 \times 6 = 72$. The results were statistically examined by methods generally used in analytical chemistry (t- and f-test,^{9 pp.52-59} oneway-ANOVA^{9 pp.67-74; 10 pp.72-83; 11 pp.259-282}) to evaluate results between and within laboratories.

The number of decimals in the measured and calculated data reported in this study are retained for calculational reasons.

2. GENERAL TOPICS AND DEFINITIONS

2.1 Calibration in quantitative analysis

Quantitative chemical analyses are based on the comparison of signals from samples with signals from known standards. This demands that we know the mathematical relation between the signal y and the content x of the standards. In ICP-AES analysis the relation is linear in over a wider range of concentration than in other analytical methods.^{3, 12 pp.6-5, 6-10, 6-16; 13-15} The relation between y and x takes the algebraic form $y = bx + a$, where b is the slope of the line and a is the intercept on the y -axis.^{9 p.86; 16,17} The calculation of the mathematical relation in calibration is generally based on linear regression, the "method of least squares", and all of the random error in the data can be assumed to assign to the dependent y signal.^{9 p.90; 17} The equations for calculating the regression parameters (a , b , s_a , s_b and r) can be found in the analytical chemistry literature.^{9 pp.86-94; 17} The product-moment correlation coefficient, r , obtained from linear regression, is widely used in an attempt to quantify linearity or "goodness of fit" to the linear model, but generally it does not give more information than is already provided by the slope and its standard error.^{9 pp.88-90; 17}

The number of calibration points and their location on the concentration axis has not been widely discussed.^{14,16} According to mathematical principles, it is known that standards should be chosen so that their mean concentration is approximately equal to the most important sample concentration and that they enclose all the expected sample concentrations.¹⁸ An increase in the number of calibration points will also narrow the confidence band, Δy , around y_0 , the signal obtained from a sample of concentration x_0 ; for 4 standards $\Delta y=7.26 s$, for 6 standards $\Delta y=3.9 s$, for 8 standards $\Delta y=3.14 s$ and for 20 standards $\Delta y=2.27 s$, where s is the estimated standard error of estimate for the regression equation.¹⁸ The more calibration points are obtained in the construction of the calibration line the better defined its slope will be.¹⁹ Moreover, if points are sampled near the origin, the intercept value may be better defined.¹⁹

2.2 Limit of detection (LOD) and limit of quantification (LOQ)¹⁹

The IUPAC definition, adopted in 1975, states that "the limit of detection, expressed as a concentration x_L , is derived from the smallest measure, y_L , that can be detected with reasonable certainty for a given analytical procedure", when the analytical relationship is expressed as $y = bx + a$. Normally in the determination of LOD blank measurements, y_B , are taken. The probability that the smallest discernible analytical signal, y_L , can be measured and not be a random fluctuation of the blank, y_B , is dependent upon how many standard deviation units y_L is from \bar{y}_B . If y_L is $3s_B$ away from \bar{y}_B , there is a 0.13% chance that a signal measured at y_L or greater would be the result of a random fluctuation of the blank signal. This small chance of error fulfills the requirement of a reasonably certain signal, and the LOD is obtained by substituting $y_L = \bar{y}_B + 3s_B$ to the regression equation and the LOQ by substituting $y_L = \bar{y}_B + 10s_B$. The LOD and LOQ obtained in this way will be a true reflection when the slope, b , and the error in blank measurements, s_B , are well-defined and the intercept, a , is essentially 0. Fig. 1 shows schematically how the LOD and LOQ values are obtained from the calibration line.

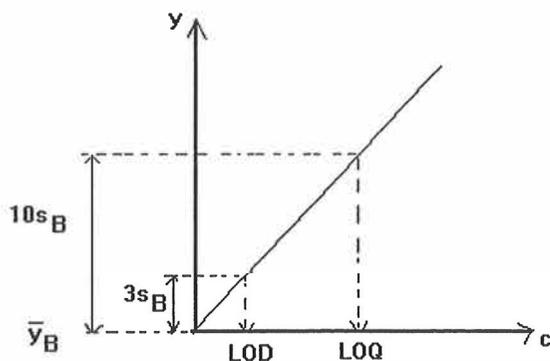


Fig. 1. Analytical calibration curve of signal, y , vs. concentration, c , showing the relationship of ks_B to the limit of detection (LOD, $k=3$) and limit of quantification (LOQ, $k=10$).

Previous models for calculating detection and quantification limits consider the error in blank measurements and analytical sensitivity (slope, b) to be well defined. A more reliable LOD is obtained by the 'graphical approach', in which the confidence interval of slope, $b \pm t_{\alpha} s_b$, is considered, where s_b is the standard deviation of the slope and t_{α} is a t distribution value chosen for the desired confidence level, α , and the degrees of freedom, ν . The t value should be chosen at the same confidence level as the value $3s_b$, i.e. 99.87%. An $\alpha=0.0005$ results in a confidence level of 99.9% for a two-tailed t distribution with $n-2$ degrees of freedom, where n is the number of calibration points used.

Error may occur also in the intercept term, and the standard deviation of the concentration has also to be considered. These are taken into account in a 'propagation of errors approach' which includes the standard deviations of the measured concentration, intercept and slope in calculating the LOD value. The LOD value calculated with the 'propagation of errors approach' is an expression of confidence value of how well the blank is known.

Our method^{I-V} for calculating the LOD and the LOQ values is based on the intercept value, a , and its standard deviation, s_a . The blank value was excluded from the linear regression calculations, because the s_b values in measurements were much higher than the standard deviations in the calibration solution measurements. When no analyte concentration is present in the calibration solutions the random error in the signal is obviously great. The error term s_a is obtained from equation^{9 pp.91-93}

$$s_a = s_{y/x} \left\{ \frac{\sum x_i^2}{n \sum (x_i - \bar{x})^2} \right\}^{1/2} \quad (1)$$

where the term $s_{y/x}$ is

$$s_{y/x} = \left\{ \frac{\sum (y_i - \bar{y})^2}{n-2} \right\}^{1/2} \quad (2)$$

For the summations in equations 1-2, i ranges from 1 to n . The term $s_{y/x}$ gives the y -residuals $y_i - \hat{y}$, where the \hat{y} values are the points on the calculated regression line corresponding to the individual x values, i.e. the 'fitted' y -values. When the regression line (b , a , s_a , s_b) is calculated from the calibration points, it is appropriate to calculate the LOD and LOQ values by using $y_L = a + 3s_a$ and $y_L = a + 10s_a$ respectively, since a can be considered as a calculated blank and s_a as the standard deviation of the calculated blank.

Table 1 shows the effects of the above calculation methods on the LOD values, when four different sets of experimental data are used.¹⁹ Table 1 shows four sets of typical experimental conditions: A, data which have a well-defined b and a ; B, data which have essentially the same s_b as in A except that the calibration points are taken far away from LOD, resulting in

Table 1. LOD values obtained from different calculation methods for four different sets of experimental data.¹⁹

Set	A	B	C	D
Calib. data (x,y)	0 , 0 0.1 , 402 1 , 6750 10 , 67000	0 , 0 10 , 67000 100 , 718000 1000 , 7600000	0 , 0 1 , 55 10 , 1810 100 , 34500	0 , 0 1 , 796 10 , 2800 100 , 60700
r	1.0000	1.0000	0.9990	0.9985
b	6710	7610	350	614
a	-79	16600	-628	-980
s_b	20	27	10	24
s_a	101	13700	545	1200
s_B	5.4	5.4	3.5	97.6
LOD-values (ppm)				
IUPAC ¹	0.002	0.002	0.03	0.5
Graphical ²	0.002	0.002	0.3	-2
Prop. of errors ³	0.05	5	5	6
Term s_a (with 0) ⁴	0.05	5	5	6
Term s_a (without 0) ⁵	0.07	7	6	9

¹ IUPAC model. ² Graphical approach. ³ Propagation of errors approach. ⁴ Standard deviation of the intercept approach, when the blank value is included in the regression calculation. ⁵ Standard deviation of the intercept approach, when the blank value is excluded from the regression calculation.

a poorly defined a and well-defined b ; C, data which have nonlinearity in the calibration curve, resulting in ill-defined b and a values; and D, data with extreme nonlinearity in the calibration curve, resulting in severe errors in both b and a values.¹⁹

For case A, the LOD values obtained with the IUPAC model and the 'graphical approach' agree well with each other, as do those obtained with the 'propagation of errors approach' and the s_a approach, which both give higher LOD values than the two first-mentioned. The deviation is due to the error associated with the intercept value, s_a . Case B illustrates the difficulties when the lowest calibration point is considerably removed from the LOD value, with the result that the nonzero intercept value is ill-defined. Thus the IUPAC model and the 'graphical approach' give erroneously low LOD values, while the remaining approaches account for this error. Cases C and D illustrate the problems with the nonlinear calibration graph, which generally produces significant s_b , s_a and a values (greater in case D). The 'propagation of errors approach' and the s_a approach give a more realistic estimate of the LOD values than the IUPAC model or the 'graphical approach'. The 'graphical approach' can even give a negative LOD when $t_{\alpha} s_b > b$; thus it is not statistically valid and can be used only for approximating LOD values.

The IUPAC model is valid only if the major source of error is in the blank measurements ($s_B^2 \gg s_a^2$ or s_b^2), and the calculated LOD values are often low. This model is very useful in comparing analytical methods and instruments. The 'propagation of errors approach' will yield LOD values consistent with the reliability of the blank measures and the signal measures of the standards. The s_a approach including the blank (see Table 1) gives the same LOD values as the 'propagation of errors approach'. When the blank value is excluded from the linear regression, the LOD values are likely to be greater and thus give more certainty in relation to choosing the smallest calibration concentration and the whole calibration range for carrying out the measurements. The LOD is thus the real concrete limit for detection.

Choosing the best calibration line can be done by verifying not only the calculated r value but also the LOD and LOQ values: the r value may be very close to 1 even if the data are patently non-linear in character. Thus the calibration curve must always be calculated and plotted to confirm linearity^{9 pp.88-90} and the decision about goodness of calibration should be

made on the basis of the r , LOD and LOQ values. When the correlation coefficient $r > 0.9998$, the calculated detection and quantification limits are usually low enough.

2.3 Experimental design and multiple linear regression

Sample concentrations are achieved by substituting the sample signal value (y) into the calibration function $y = bx + a$.^{9 pp.94-96} This is called interpolation, when the measured values are within the range of calibration data.¹⁷ The obtained concentration of the unknown sample is also a linear function of the measured signal, when calibration is confined within a linear range. Thus it is possible to evaluate the interferences of sample constituents on interpolated data using a well-defined experimental design as follows:

- 1) Evaluate the possible elements of the sample constituent which may interfere with the analyte element. In making this decision the analyst may use his own experience of analytical interferences of elements, known interferences reported in the analytical literature as well as wavelength tables, which gives the possible interfering lines close to the analyte line(s) examined.
- 2) Approximate the concentrations of the possible interfering elements in sample solutions, when those have been prepared and diluted according to the sample preparation instructions.
- 3) Decide the levels of each of the interfering elements to be added to the real sample solutions. Calculate the interference matrix (number of elements \times levels of concentration), so that the levels of the added elements correlate by less than 0.2 with each other. The added interference matrix is thus mathematically independent. Typically in interference studies the used concentration of the matrix element is the approximated level of the base concentration or its multiple, and its effect on the analyte element is measured separately. In the procedure described, the effects of the interfering elements are studied without separation, and thus five concentration levels are needed of each interfering element to achieve reliable observations.
- 4) It has turned out that for n interfering elements included in interference matrix one must measure $3n$ matrix element solutions to obtain an adequate amount of data for the equations used to solve the equation group. Matrix elements are added at concentrations found using the correlation models to actual sample solutions, and the concentration of

the analyte element is measured. Each of the 3n solutions made contains variable concentrations of matrix elements which do not correlate significantly with each other and virtually equal concentrations of the analyte element, i.e the concentration which came from the base sample.

- 5) The concentration of the analyte element is obtained from the linear calibration graph by interpolation. Thus the measured concentrations of the analyte element in the solutions are also expected to be linear with the matrix constituents. Hence it is possible to calculate the effects of the matrix elements on the analyte element by solving the equation group using multiple linear regression.^{11 pp.330-357}

Multiple linear regression extends bivariate regression by incorporating multiple independent variables, and the model can expressed in the examined case as

$$y_i = \beta_0 + \beta_1 x_{1i} + \beta_2 x_{2i} + \dots + \beta_p x_{pi} + e_i \quad (3)$$

where y_i (dependent variable) is the measured concentration of the analyte element from sample matrix solution i ; x_{pi} (independent variable) indicates the concentration of the p th independent interfering element in sample matrix solution i ; β terms are unknown parameters and e_i terms are independent random variables with normal distribution.^{11 p. 330}

It is possible to evaluate the effects of each of the added interfering element on the examined analyte element when the concentration of the analyte element has been measured and the independent interfering matrix elements concentrations are known. Multiple regression lines can be calculated with this known information, and by substituting the real concentrations of the interfering matrix elements in the base sample into the obtained multiple regression line the concentration corrected for interference is found. Finally, it is convenient to evaluate the goodness of the used analytical method, when the base concentrations of the examined analyte in the samples are measured and the interference-corrected concentration is calculated: when the difference between them is of about the same magnitude as the acceptable error (with ICP-AES $< \pm 5\%$), the measurements can be done without sample constituent interference.

2.4 Spectral and interelement effects

The effects of interfering matrix elements on the element analyzed can be evaluated as either spectral effects or interelement effects. Four kind of spectral effects exist: simple background shift, sloping background shift, direct spectral overlap and complex background shift.^{12 pp.4-4} 4-14 The effect of the matrix element is considered as a spectral effect when one or more of its wavelengths is found within ± 0.2 nm of the analyte line of the element being examined. Spectral effects cause changes in the background: simple background shift may occur over a 0.5 nm range on each side of the analyte line; sloping background shift may occur over a range of at least 0.2 nm on each side of the analyte line; direct spectral overlap occurs when two spectral lines have a direct coincidence; and complex background shift may occur over a 0.5 nm range on either side of the analyte line.^{12 p.4-4}

The effect of the observed interfering matrix element on the analyte element is considered an interelement effect when it is not a clear spectral effect. It may include some of the characteristics of spectral effects and may also include chemical effects.

3. EXPERIMENTAL

3.1 Laboratory equipment and reagents

All the laboratory glasses used (beakers, flasks, burettes, pipettes, watch glasses, etc.) were acid-washed by soaking overnight in 10% nitric acid solution, after which they were thoroughly rinsed with water. All the reagents used in the experiments were at least analytical reagent grade, and in solution preparation as in rinsing the laboratory glasses ultrapure water was used.

3.2 Dissolution of fertilizer samples

Both water-soluble (WS) and acid-soluble (AS) dissolutions for B and Mg and AS dissolution for Fe and Ca were done according to AOAC official final action methods.^{8,11,11,v} The

instructions for the WS and AS dissolutions for S are given in paper IV.

3.3 Samples for interference studies

Stock solutions of each of the seven possible interfering elements were prepared from pure metal or proper salt.^{I-V} Each interfering element was added to the real fertilizer sample solutions at five concentration levels. The lowest added concentration of each element was the average concentration present in the fertilizer under examination and the highest added concentration was five times the lowest.

Seven possible interfering elements at five concentration levels yields 78125 possible combinations of concentrations. Using correlation models a subset of 21 combinations of matrix element concentrations is derived, which is an adequate sample of all the possible combinations to yield reliable observations. Additions to the fertilizer sample solutions were done according to the calculated mathematically independent ($r < 0.2$) interference matrix^{I-V} during preparation, before they were diluted to volume. The concentration of the analyte element was not affected: it came from fertilizers equally weighed for each of the 21 sample solutions. One further fertilizer sample solution with no interfering element additions was made up. Thus the interference calculations were based on the measurements of 22 solutions.

3.4 Calibration

The ICP-AES instruments were calibrated using five calibration standard solutions made from pure metal or proper salt of analytical reagent grade and one blank solution. The standards included regular increments of the analyte element. The acid concentration of the standards was adjusted to the same level as in the samples.

The standards were also supplemented by a NPK solution called the 'fertilizer matrix solution' for matrix-matching the standard solutions with those of the samples.^{I-V} The added fertilizer matrix solution corresponds to fertilizer NPK 15-15-15 when 1 g of it is dissolved in 200 ml of water. The calibration standard solutions contained N at 750 mg/l, K at 625 mg/l and P at 326 mg/l. This fertilizer matrix solution is used in one Finnish fertilizer laboratory, and it has

proved useable in analyzing fertilizer elements from a wide variety of fertilizer compositions.

The calibration solutions were made up in a similar way both in the collaborative studies and in the interference studies: they contained N, K and P at the concentrations mentioned above but not other possible interfering elements, as much acid as in the sample solutions and an analyte element in regular increments.

3.5 ICP-AES measurements

In our laboratory a Perkin-Elmer ICP 1000/2000 apparatus was used. The instrument parameters (viewing height, nebulizer flow and plasma power) were optimized. Table 2 gives the wavelengths and optimized ICP-AES instrument parameters used in the measurements. The auxiliary gas flow was 1.0 l/min and the plasma gas flow was 15 l/min in every case.

In sulfur determination the optics and torch department were fast purged with nitrogen for half an hour after which a normal purge was maintained.

Each solution was aspirated to plasma with a one-minute read delay time and three replicates were measured. The calibration solutions were introduced to plasma in order of concentration, starting with the highest and finishing with the blank solution. The linearity of the calibration graph was checked by plotting the graph. Goodness of calibration was also checked by measuring the middle standard solution, and if the difference between the measured concentration and known concentration was <5% the calibration was accepted. In the long term measurements the stability of calibration was also checked at regular intervals with standards close to those of sample concentrations.

Table 2. The wavelengths and optimized ICP-AES parameters used in the fertilizer analysis.

Element	Wavelength [nm]	Viewing height [mm]	RF power [W]	Nebulizer gas flow [l/min]
B	208.893	12	900	1.130
	208.959	10	820	1.090
	249.678	9	820	1.180
	249.773	9	800	1.240
Mg	202.582	11	680	0.840
	279.553	7	640	1.190
	285.213	7	640	1.180
	383.826	14	660	1.180
Fe	238.204	11	920	0.990
	239.562	11	660	1.170
	240.488	9	660	1.150
	259.940	7	640	1.170
S	180.731	15	860	1.160
	182.037	15	860	1.160
	182.625	15	860	1.160
Ca	317.933	15	880	1.150
	393.366	15	860	1.160
	396.847	15	860	1.160
	422.673	15	1340	0.840

Table 3 shows the best calibration data at the best wavelengths found and also at those wavelengths which were used in both the collaborative and the interference studies.^{I-V}

Table 3. The best calibration data obtained in the determination of nutrients at different wavelengths.

Wavelength	Sample	$y=(b\pm s_b)x + (a\pm s_a)$	r	LOD ^a	LOQ ^b
B 249.678	WS-B	$(1093\pm 11)x + (574\pm 179)$	0.9999	0.490	1.635
	AS-B	$(1043\pm 8)x + (393\pm 139)$	0.9999	0.399	1.328
B 249.773	WS-B	$(1867\pm 10)x + (831\pm 173)$	1.0000	0.278	0.928
	AS-B	$(1537\pm 12)x + (781\pm 194)$	0.9999	0.379	1.263
B 208.959*	WS-B	$(803\pm 7)x + (444\pm 118)$	0.9999	0.441	1.471
	AS-B	$(901\pm 10)x + (1284\pm 174)$	0.9998	0.578	1.928
Mg 383.826*	WS-Mg	$(14\pm 4)x + (-6\pm 1)^c$	1.0000 ^c	0.148 ^c	0.495 ^c
	AS-Mg	$(14\pm 7)x + (-2\pm 3)^c$	1.0000 ^c	0.552 ^c	1.839 ^c
Fe 238.204*	AS-Fe	$(2483\pm 25)x + (70\pm 167)$	0.9998	0.202	0.674
Fe 239.562	AS-Fe	$(303\pm 1)x + (24\pm 8)$	1.0000	0.074	0.247
Fe 259.940	AS-Fe	$(271\pm 2)x + (8\pm 13)$	0.9999	0.148	0.495
S 180.731*	WS-S	$(597\pm 5)x + (-773\pm 761)$	0.9999	3.823	12.743
	AS-S	$(533\pm 5)x + (-2039\pm 1113)$	0.9999	6.265	20.884
S 182.037	WS-S	$(193\pm 2)x + (-277\pm 253)$	0.9999	3.926	13.085
	AS-S	$(197\pm 1)x + (-13\pm 284)$	0.9999	4.316	14.386
Ca 396.847*	AS-Ca	$(7047\pm 51)x + (229\pm 853)$	0.9999	0.363	1.211

^a Limit of detection, mg/l. ^b Limit of quantification, mg/l. ^c Three calibration solutions. * The best wavelength found.

4. MAIN RESULTS AND OBSERVATIONS

4.1 Collaborative studies

WS and AS boron, magnesium and sulfur and AS iron were determined in two fertilizers in four ICP-AES laboratories. Each laboratory used their own optimized ICP-AES procedure and thus wavelength selection was not the same between laboratories. The measurements were done in three groups, each of which comprised six sub-samples. t- and f- test values were

calculated for each sample group in each laboratory to examine whether the results obtained were the same and thus had good repeatability.^{I-V} Oneway-ANOVA calculations were also done for the 18 values obtained in each laboratory in order to test whether the results between laboratories were the same and thus had acceptable reproducibility.^{I-IV}

Generally, variation within each laboratory was smaller in the AS results than WS results, and variation between laboratories smaller in the WS results than AS results, irrespective of the wavelength used. In other words, repeatability was better with AS measurements and reproducibility with the WS measurements. The oneway-ANOVA calculations showed that the concentrations of AS-Fe (NPK 20-4-8) and WS-S (both fertilizers) measured in the laboratories were equal.^{I-IV}

The differences between the determination groups in each laboratory were due to random errors in calibration: measured sample concentrations between separate calibrations varied by 5.7% and 7% on average for fertilizers NPK 25-4-4 and NPK 20-4-8, respectively. Separate calibrations were used because of the long time interval between measurements groups, and freshly made up calibration solutions were used in each of the measurements. Generally, the measurements of replicate samples belonging to the same group should be done with the same calibration to avoid additional errors caused by random errors in calibration.

Differences between laboratories may have been caused by systematic errors either in sample preparation or in the measurements. Hence we made up one pre-digested test AS-S sample from fertilizer NPK 25-4-4 and mixed calibration solutions for the measurement of Fe, B and S, which were divided into four parts and sent to each laboratory. The Fe, B and S concentrations were measured six times in the homogenous test solution and the results are shown in Table 4. For the sake of comparison the results of AS-B, AS-Fe and AS-S from the collaborative study is also shown in Table 4. As can be seen from Table 4 the B and S results obtained from the laboratory-prepared solutions in the collaborative studies include the B and S results from the test solution. The Fe results are not comparable, because the sample preparation methods (AS-S and AS-Fe) differed markedly from each other. No systematic errors in sample preparation by the laboratories were otherwise evident. Thus the differences between the laboratory results are due to measurements at different wavelengths.

Table 4. Concentration of acid-soluble B, Fe and S from homogenous test sample and from samples made in collaborative studies in each laboratory.

Sample	Laboratory	Wavelength [nm]	Concentration [% by wt]	
			Collab. sample ^a	Test sample ^b
AS-B	L1	249.773	0.0295 ± 0.0023	0.0278 ± 0.0001
	L2	249.683	0.0285 ± 0.0007	0.0275 ± 0.0002
	L3	249.68	0.0264 ± 0.0012	0.0274 ± 0.0001
	L4	249.678	0.0260 ± 0.0010	0.0265 ± 0.0016
AS-Fe	L1	238.204	0.139 ± 0.006	0.140 ± 0.001
	L2	259.956	0.143 ± 0.002	0.134 ± 0.0003
	L3	259.94	0.146 ± 0.004	0.134 ± 0.0004
	L4	239.562	0.150 ± 0.003	0.133 ± 0.001
AS-S	L1	182.034	1.76 ± 0.079	1.78 ± 0.019
	L2	180.732	1.82 ± 0.034	1.77 ± 0.025
	L3	180.73	1.72 ± 0.049	1.74 ± 0.008
	L4	182.037	1.80 ± 0.148	1.67 ± 0.014

^a Mean and standard deviation of 18 determinations.

^b Mean and standard deviation of 6 determinations.

The error of any individual measurement in a laboratory independent of the wavelength used can be estimated by the equation $t s_d \sqrt{2}$, where s_d is the standard deviation and t is the t-distribution critical value with $2n$ degrees of freedom.^{10 pp.24-25} When using the collaborative data ($n=72$), the measurement errors were within 19-28 % for boron, 12-17 % for magnesium, 13-18 % for sulfur and 8-11 % for iron, irrespective of the used wavelength. The fact that almost all the values obtained from every sample digestion were within these calculated errors means that acceptable oneway-ANOVA results are obtained (Table 5A). Further error estimation is obtained by reducing the above error until the acceptable oneway-ANOVA boundary is reached. Moreover, clear outlier values are omitted from the calculations. Table 5B shows the boundary errors which yield acceptable oneway-ANOVA calculations independent of the wavelength used when whole sample ($n=72$) is included or when the outlier values are omitted.^{11 pp.177-179}

Table 5. Oneway-ANOVA calculations from collaborative data using either the maximum calculated standard deviation (A) or the boundary standard deviation which yields acceptable oneway-ANOVA results (B).

	Fertilizer/ Sample	20-4-8			25-4-4		
		n ^a	s _d [%] ^b	F _{Prob} ^c	n ^a	s _d [%] ^b	F _{Prob} ^c
A	WS-B	72	28.2	0.5869	72	22.6	0.7167
	AS-B	72	19.3	0.2706	72	20.8	0.2088
	WS-Mg	72	12.2	0.3547	72	13.2	0.3015
	AS-Mg	72	17.2	0.1657	72	15.8	0.4611
	AS-Fe	72	8.21	0.9198	72	11.4	0.3759
	WS-S	72	13.3	0.7898	72	15.3	0.7891
	AS-S	72	18.9	0.4134	72	15.2	0.7014
B	WS-B	68	10.5*	0.0270	69	11.6*	0.0918
	AS-B	65	7.9	0.0209	65	9.0	0.0054
	WS-Mg	72	7.5	0.0407	72	8.0	0.0242
	AS-Mg	62	8.5	0.0221	67	8.5	0.0440
	AS-Fe	72	3.7*	0.2899	72	8.2	0.0450
	WS-S	72	7.4*	0.0348	72	9.5*	0.0352
	AS-S	64	6.2	0.3373	72	6.2	0.0444

^a Number of measurement data, total n=72.

^b Standard deviation for n measurement data calculated as percentages from the mean of n measurement data.

^c Probability of F statistic according to oneway-ANOVA calculations.

* Original s_d which yields acceptable oneway-ANOVA result without estimation.

4.2 Interference studies

The interference of seven typical fertilizer matrix elements on the determination of B^I , Mg^{II} , Fe^{III} , S^{IV} and Ca^V were examined by adding them into real fertilizer sample solutions at five concentration levels {(7x5)-matrix}. The concentrations of the above-mentioned elements were measured by ICP-AES at 3-4 different wavelengths from fertilizer sample solutions all of which contained the matrix elements and same fertilizer base. In addition, fertilizer sample solutions which did not contain any added matrix elements were measured to obtain the base concentration of the analyte element. When the base concentration of the analyte element is known it is possible to find out how the added matrix elements at variable concentrations influence the analyte element. The effects of the added matrix elements were calculated by multiple linear regression. Multiple linear regression is a suitable method, since calibration is confined to a linear range ($r > 0.9998$). This is very high demand when six-point calibration is used.

Table 6 shows the interfering elements found in this study by multiple linear regression (columns 3 and 4) for each sample type and their rough classification as spectral or interelement effects (columns 5 and 6). Table 6 also shows earlier observed interferences from the analytical literature (column 7). As can be seen from Table 6 the interelement effects are mainly caused by easily ionizable elements, EIE, (Ca, K, Na, Mg). These elements are highly ionized in the ICP and they exhibit very high line/background ratios even at relatively low concentrations or yield line-rich spectra.^{24,25} The spectral effects are caused mainly by P, S, B and Fe.

The effect of EIEs in analytical flame spectroscopy and in arc discharge have been well characterized.²⁶ Addition of EIE has the effect of increasing the electron density in flames, and the ionization equilibrium for the analyte atom, ion and electrons shifts toward the neutral atom species, causing enhancement of neutral atom line emission. In an arc discharge the addition of EIE increases the electrical conductivity of the arc but leaves the thermal conductivity essentially unchanged. The arc responds to this by a lowering in temperature such that the power supplied to the arc is once again balanced by energy loss due to thermal conduction. This leads to a suppression of the ionization equilibria, a reduction in the excited

Table 6. Interference elements found^{I-V} by multiple linear regression for each sample type and their classification as spectral or interelement effects.

λ [nm]	Sample	20-4-8	25-4-4	Spectral	Interelement	Earlier known ^a
B 208.893	WS	Ca,Fe,P	P	Fe	Ca,P	
	AS	Ca,K,Mg	P		Ca,K,Mg,P	
B 208.959	WS	Ca,Fe,P	P	Fe	Ca,P	Ca, Fe ¹²
	AS	Ca,K	K,P		Ca,K,P	
B 249.678	WS		K,P	P	K	K, ² Fe ²⁰
	AS		K,P	P	K	
B 249.773	WS	Fe	K,Fe	Fe	K	K, ^{1,4} Fe ^{12,20}
	AS		K,P	P	K	
Mg 202.582	WS	Fe,S	K,P	Fe,P,S	K	Ca, Mn ²³
	AS	Ca	Mn,Na,S	S	Ca,Mn,Na	
Mg 279.553	WS	Ca,Na	K,Na		Ca,K,Na	K ⁴
	AS	Ca,K,Na	Ca,K,S		Ca,K,Na,S	
Mg 285.213	WS	P	K,Na,P,S	Na	K,P,S	Ca, Mn, ²³ no P ³
	AS	Ca,K	Mn		Ca,K,Mn	
Mg 383.826	WS	Ca,Mn,Na,S	K,Na	Ca,Mn,S	K,Na	Ca, Mn ²³
	AS	Na	Fe,S	Fe,S	Na	
Fe 238.204	AS	B,Ca,K	P		B,Ca,K,P	Ca, ¹² none ⁵
Fe 239.562	AS	Ca	K,P	Ca	K,P	Ca ¹²
Fe 240.488	AS	Ca	K,P		Ca,K,P	
Fe 259.940	AS	K,S	K		K,S	K ⁴
S 180.731	WS	Ca,Mg,P	Ca,K,P	Ca	K,Mg,P	Ca, ^{12,21} Mg ¹²
	AS	Ca,K,P	K,P	Ca	K,P	
S 182.037	WS	B,Mg	K,P		B,K,Mg,P	Mg, ¹² no K,Mg,P ²²
	AS	K,Mg,P	K		K,Mg,P	
S 182.625	WS	B,K	B,Ca,K	B	Ca,K	B, Ca ¹²
	AS	B		B		
Ca 317.933	AS		K,S		K,S	
Ca 396.847	AS		K,S		K,S	
Ca 422.673	AS		B,K	B,K		K ⁴

^a no: mentioned elements have not been observed to cause interference; none: no interferences were encountered

level population, and increased residence times of the analytes in the arc. The combined effects produce suppressions and enhancements of line intensities, depending on the type of species (atoms or ions) and their ionization potentials, and on the excitation potentials of the lines.

The situation is not quite so well defined in ICP-AES, but both the plasma operating conditions (observation height, RF power, aerosol flow rate) and the complexity of the EIE influence causes contribute to the overall effect of EIE's in ICP-AES.²⁶ This explains the earlier disagreement among investigators, which appear as inconsistent data: some investigators observed analyte emission 'enhancement', some 'depressions' and some 'no effect'. In the lower part of the plasma analyte channel (up to 15-20 mm above the load coil) enhancements of analyte sensitivity for both the atom and ion lines are caused by the alkali metal matrix, which in turn is attributed to increased collisional excitation.^{26,27} The process of ambipolar diffusion becomes increasingly important above about 12 mm in the analyte channel, leading to a suppression of sensitivity higher than 15-20 mm for both the atom and ion lines.^{26,27} It has been found that in running analyses under the respective recommended conditions of most commercially produced ICP-AES instruments the matrix effects result in suppression for most elements.²⁷

The matrix effect does not disappear when optimizing the operating and observation conditions, but it can be minimized and its effect on the analyte element can be evaluated by the procedure described in this examination. The matrix effect occurs mainly in the plasma rather than in the nebulizer.^{26,27} However, nebulizer matrix effects play a role when the physical properties of solutions change grossly, but they are still not the dominant interference mechanism.^{26,27} In this study the optimized ICP-AES parameters (Table 2) were used, and all of the measurements of the analyte element of interest were done at the optimal observation height. The interferences found in this study and the interferences found by other investigators do not allow of exact comparison due the facts described above. Nonetheless, the interferences found in this study are highly the same as known earlier while also including some new interferences.

Blades and Horlick²⁶ have showed that the effect of different EIEs depends on their ionization potentials: the magnitude of the enhancement increases with the decreasing ionization potential of the EIE at the lower observation heights (< 15.5 mm) when different EIEs are studied separately. The first ionization potentials of EIEs in decreasing order are Mg 7.64 V, Ca 6.11 V, Na 5.14 V and K 4.34 V.^{28 p.E-68} In this work the sample solutions contained different EIEs together in same solution, and their effects on the examined element are considered in the light of Blades' and Horlick's²⁶ conclusion: when the EIE effect is observed together their strengths mainly follows the observation of Blades and Horlick (see Table 7). In our opinion, in sample solutions of variety matrices it is important to know how combinations of different matrix elements influence the determination of the analyte element of interest, because they all are present in the made-up samples. The total effect of different matrix elements may be one of strengthening, weakening or compensating for each other, and studying the interferences of matrix elements separately would yield to erroneous conclusions.

Table 7 shows the total effects of the observed interference elements on the analyte element concentration. The values are calculated from the multiple linear regression lines^{1-V} by substituting the real concentrations of the interference elements in the fertilizer base into the multiple regression equations. As can be seen from Table 7 the matrix interference experimental design shows the effects of the matrix constituents on the element under examination and in most cases these are quite small. Thus at the matrix constituent concentration levels in the examined fertilizer bases the total combinations of the matrix effects are in most cases negligible and do not significantly change the measured concentration of the element of interest: the determination is interference free. One must keep in mind that in quite many cases the interferences weaken or compensate for each other. When they strengthen each other, significance interferences are observed.

Table 7. Proportional magnitudes of interference effects and the total effect percentages of the intercept value calculated from the obtained multiple linear regression lines.^{1-V}

Line [nm]	Sample ^a	Fe ^b	Ca ^b	P ^b	K ^b	Mg ^b	S ^b	Na ^b	Total effect [%]
B 208.893	WS(1)	-2	-2	-4					-2.37
	AS(1)		-6		-7	5			-1.90
	WS(2)			-4					-1.62
	AS(2)			-4					-1.42
B 208.959	WS(1)	-2	-3	-7					-3.45
	AS(1)		-5		-8				-3.00
	WS(2)			-3					-1.24
	AS(2)			-9	2				-2.56
B 249.678	WS(2)			-7	6				-0.37
	AS(2)			-14	9				-1.62
B 249.733	WS(1)	10							+2.39
	WS(2)	5			3				+2.80
	AS(2)			-11	10				-0.30
Mg 202.582	WS(1)	396					-305		+1.22
	AS(1)		208						+2.40
	WS(2)			112	-138				-0.51
	AS(2)						55	-80	+0.41
Mg 279.553	WS(1)		600					280	+15.7
	AS(1)		260		788			152	+16.6
	WS(2)				307			112	+11.4
	AS(2)		65		154		49		+4.63
Mg 285.213	WS(1)			465					+6.74
	AS(1)		219		549				+9.43
	WS(2)			136	179		-75	172	+10.6
Mg 383.826	WS(1)		144				-248	176	+0.96
	AS(1)							144	+1.51
	WS(2)				120			104	+5.25
	AS(2)	152					67		+3.69

^a (1), fertilizer NPK 20-4-8, and (2), fertilizer NPK 25-4-4. ^b Multiplier 10⁻⁴.

Table 7. Continued.

Line [nm]	Sample ^a	Fe ^b	Ca ^b	P ^b	K ^b	Mg ^b	S ^b	B ^b	Total effect[%]
Fe 238.204	AS(1)		-25		-25			3	-2.40
	AS(2)			-39					-2.28
Fe 239.562	AS(1)		24						+1.20
	AS(2)			-84	80				-0.24
Fe 259.940	AS(1)				66		52		+5.80
	AS(2)				73				+4.77
Fe 240.488	AS(1)		46						+2.12
	AS(2)			-77	92				+0.99
S 180.731	WS(1)		301	-128		-250			-0.28
	AS(1)		290	-230	240				+1.01
	WS(2)		230	-97	63				+1.21
	AS(2)			-378	262				-0.67
S 182.037	WS(1)					-215		-128	-1.24
	AS(1)			-383	670	-381			-0.34
	WS(2)			-97	58				-0.24
	AS(2)				297				+1.82
S 182.625	WS(1)				-1361			6061	+21.1
	AS(1)							2450	+9.69
	WS(2)		-440		-330			6618	+45.8
Ca 396.847	AS(2)				-47		-47		-0.57
Ca 317.933	AS(2)				-66		-45		-0.70
Ca 422.673	AS(2)				-149			-157	-1.91

^a (1), fertilizer NPK 20-4-8, and (2), fertilizer NPK 25-4-4. ^b Multiplier 10⁻⁴.

Table 8 shows the concentrations of each analyte element calculated by multiple linear regression and determined by ICP-AES. Table 8 also shows the differences in the percentages of determined values. When these percentage values are $< 5\%$ of the determined values, i.e. below the acceptable level of error, the determination can again be said to be interference free. Thus Tables 7 and 8 support each other. In Tables 7 and 8 value pairs which confuse each other can be seen, for example the value pairs from the last column of Tables 7 and 8 (-0.37,-13.62) for WS(2) at line B 249.678 and (+15.7,-17.87) for WS(1) at line Mg 279.553. These are examples of where either a small or high correction leaves the determined and the calculated concentrations far from each other. This can be explained by the fact that the raw determined concentration is highly influenced by the complex fertilizer constituent matrix and hence the multiple linear regression corrected value would be near the true concentration.

The best analytical wavelengths found in this study for the determination of fertilizer elements are indicated by an asterisk in Table 8. The best wavelengths are selected by combining the calibration data and the results from the interference studies at different wavelengths. The most important criteria in the calibration data when selecting the best wavelengths were linearity of the calibration line and LOD and LOQ values as low as possible. In the case of the interference studies the most important criterion was an interference-free determination. By combining these criteria the best wavelength can be found.

Table 8 also shows the importance of equal wavelength selection, especially in collaborative ICP-AES studies. The concentrations measured from the same dissolution would be markedly different at different wavelengths. Table 9 collects the percentage differences between the highest and the lowest means determined at different wavelengths both in the interference studies and in the collaborative studies. The percentage differences are not same in these two studies, because the wavelengths used differed in part. The wavelengths used in the interference studies, for example, are shown in Table 8. In the collaborative studies the

Table 8. Determined and calculated levels of fertilizer elements and the calculated differences.

Line [nm] ^a	Sample	Determined [%] ^b	Calculated [%]	Percentage difference of the determined values
B 208.893	WS(1)	0.0337±0.0011	0.0329	+2.37
	AS(1)	0.0412±0.0035	0.0414	-0.49
	WS(2)	0.0233±0.0005	0.0243	-4.29
	AS(2)	0.0264±0.0004	0.0276	-4.55
B 208.959 ^c	WS(1)	0.0330±0.0013	0.0334	-1.21
	AS(1)	0.0389±0.0016	0.0420	-7.97
	WS(2)	0.0233±0.0006	0.0237	-1.72
	AS(2)	0.0270±0.0007	0.0266	+1.48
B 249.678	WS(1)	0.0372±0.0012	-	-
	AS(1)	0.0457±0.0022	-	-
	WS(2)	0.0235±0.0004	0.0267	-13.62
	AS(2)	0.0276±0.0005	0.0304	-10.14
B 249.773	WS(1)	0.0380±0.0016	0.0427	-12.37
	AS(1)	0.0461±0.0023	-	-
	WS(2)	0.0242±0.0002	0.0295	-21.90
	AS(2)	0.0278±0.0005	0.0334	-20.14
Mg 202.582	WS(1)	0.7638±0.0289	0.7577	+0.80
	AS(1)	0.8917±0.0237	0.8867	+0.56
	WS(2)	0.4815±0.0174	0.5023	-4.32
	AS(2)	0.6021±0.0222	0.6046	-0.42
Mg 279.553	WS(1)	0.5496±0.0271	0.6478	-17.87
	AS(1)	0.8225±0.0294	0.8411	-2.26
	WS(2)	0.2767±0.0078	0.4082	-47.52
	AS(2)	0.4533±0.0174	0.6055	-33.58
Mg 285.213	WS(1)	0.6240±0.0232	0.7362	-17.98
	AS(1)	0.8657±0.0294	0.8913	-2.96
	WS(2)	0.3197±0.0101	0.4290	-34.19
	AS(2)	0.4960±0.0200	0.5500	-10.89

Table 8. Continued.

Line [nm] ^a	Sample	Determined [%] ^b	Calculated [%]	Percentage difference of the determined values
Mg 383.826 [*]	WS(1)	0.7391±0.0403	0.7581	-2.57
	AS(1)	0.9648±0.0317	0.9710	-0.64
	WS(2)	0.4291±0.0146	0.4494	-4.73
	AS(2)	0.6040±0.0243	0.6154	-1.89
Fe 238.204 [*]	AS(1)	0.1945±0.0057	0.1909	+1.85
	AS(2)	0.1614±0.0031	0.1668	-3.35
Fe 239.562	AS(1)	0.1986±0.0051	0.2022	-1.81
	AS(2)	0.1608±0.0050	0.1684	-4.73
Fe 259.940	AS(1)	0.1785±0.0038	0.2151	-20.50
	AS(2)	0.1284±0.0025	0.1602	-24.77
Fe 240.488	AS(1)	0.1982±0.0031	0.2219	-11.96
	AS(2)	0.1433±0.0044	0.1530	-6.77
S 180.731 [*]	WS(1)	2.8880±0.0152	2.7857	+3.54
	AS(1)	3.0148±0.0379	3.0105	+0.14
	WS(2)	1.6730±0.0145	1.6350	+2.27
	AS(2)	1.7114±0.0127	1.7257	-0.84
S 182.037	WS(1)	2.7937±0.0372	2.7288	+2.32
	AS(1)	3.0093±0.0242	2.7427	+8.86
	WS(2)	1.6710±0.0374	1.5974	+4.40
	AS(2)	1.7059±0.0176	1.6597	+2.71
S 182.625	WS(1)	2.7994±0.0386	2.7004	+3.54
	AS(1)	2.8893±0.0364	2.7732	+4.02
	WS(2)	1.6768±0.0252	1.8624	-11.07
	AS(2)	1.6374±0.0052	-	-

Table 8. Continued.

Line [nm] ^a	Sample	Determined [%] ^b	Calculated [%]	Percentage difference of the determined values
Ca 393.366	AS(1)	2.8979±0.0179	-	-
	AS(2)	1.7003±0.0170	-	-
Ca 396.847*	AS(1)	2.9511±0.0199	-	-
	AS(2)	1.7114±0.0301	1.6314	+4.67
Ca 317.933	AS(1)	2.8749±0.0211	-	-
	AS(2)	1.7083±0.0194	1.5771	+7.68
Ca 422.673	AS(1)	2.8945±0.0480	-	-
	AS(2)	1.6923±0.0303	1.5724	+7.09

^a The best analytical wavelength found in this study is indicated by an asterisk*.

^b Mean and standard deviation of 13 determinations for boron and 6 for the others.

wavelengths used were 249.773 nm, 249.683 nm, 249.678 nm and 249.68 nm for boron; 383.826 nm, 280.270 nm and 383.23 nm for magnesium; 238.204 nm, 259.956 nm, 239.562 nm and 259.94 nm for iron; and 182.034 nm, 180.732 nm, 182.037 nm and 180.73 nm for sulfur.

The differences in results between the laboratories which participated in the collaborative studies were not due to systematic errors in sample preparation. This was confirmed by analyzing the test sample in each of the participating laboratories. Thus the differences between laboratory results are due to the different wavelengths used in the different laboratories, as fertilizer matrix effect patterns vary from one wavelength to another. Spectral and interelement effects also occur in ICP-AES measurements, although earlier it was thought otherwise. This demands more from the measurements: wavelength selection and the optimization of instrument operating parameters will play a greater role than earlier in the analysis of varying sample matrices in order for the interferences to be minimized.

Table 9. Percentages differences between the highest and the lowest mean measured at different wavelengths in the interference and collaborative studies.

Sample ^a	Difference [%] in interference studies	Difference [%] in collaborative studies
WS-B (1)	13.16	11.91
AS-B (1)	15.62	10.57
WS-B (2)	3.72	7.95
AS-B (2)	5.04	11.76
WS-Mg (1)	28.04	6.55
AS-Mg (1)	14.75	11.52
WS-Mg (2)	42.53	7.24
AS-Mg (2)	24.95	8.08
AS-Fe (1)	10.12	1.59
AS-Fe (2)	20.45	7.53
WS-S (1)	3.27	3.41
AS-S (1)	4.16	10.07
WS-S (2)	0.35	4.59
AS-S (2)	4.32	5.38
AS-Ca (1)	2.58	not measured
AS-Ca (2)	1.12	not measured

^a (1) represents fertilizer NPK 20-4-8; (2) fertilizer NPK 25-4-4.

As can be seen from Tables 9 and 5B oneway-ANOVA calculations give acceptable results for all the measurement data ($n=72$) when the difference between the mean values of the laboratories at different wavelengths in the collaborative study is $<5\%$. When the difference between the laboratory means are about $5-7.5\%$, oneway-ANOVA calculations yield acceptable results in estimations of standard deviations. When the difference between laboratory means is $>7.5\%$, acceptable oneway-ANOVA results are obtained by omitting outlier and extreme values^{11 pp. 177-179} [i.e. cases with values that are more than 3 box-lengths from the upper or the lower edge of the box in the Explore procedure] and estimating the standard deviations. Fig. 2 shows schematically the definition of the extreme and the outlier values obtained by the SPSS' Explore procedure.^{11 p. 178} Unequal wavelength selection in the collaborative measurements yields apparently equal results when the differences in level in the measured concentrations are $< 5\%$ between the analytical wavelengths used.

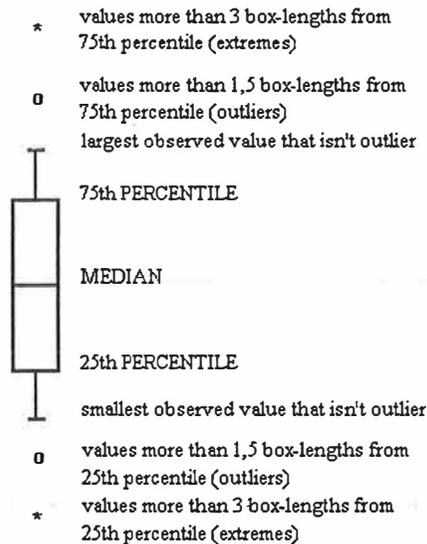


Fig. 2. Annotated sketch of a boxplot.

5. CONCLUSIONS

The limit of detection and limit of quantification values were calculated by the s_a approach excluding the blank value. The LOD and LOQ values calculated by this method were considerably greater than those calculated by IUPAC model, but they permit more certainty in choosing the smallest calibration concentration as well as the whole calibration range. The criterion for the linearity of the calibration line was $r > 0.9998$. This was a very high demand from the point of view of using six-point calibration, but it yields an acceptable level of certainty for the LOD and LOQ values and concentration measurements.

The inter-laboratory differences in the collaborative studies were due to random errors in calibration. Variation in the measured concentration levels between different calibrations was found to be 5.7% and 7% on average, respectively, for the fertilizers NPK 25-4-4 and NPK 20-4-8. Nonetheless quite good repeatability was achieved. The differences in the results between laboratories were due to the different wavelengths used in those laboratories. The calculated errors needed to achieve the same results between laboratories independent of the wavelength used were 8-12% for B, 7.5-8.5% for Mg, 3.7-8% for Fe and 6.2-9.5% for S.

The interference studies at 3-4 analytical wavelengths for each of the analyzed elements indisputably showed the differences in the measured concentrations to be due to the changing interference pattern from one wavelength to another. Calculation of interferences was done using the multiple linear regression procedure, which is permissible when calibrations are done in the linear range. The interference elements found agreed in great deal with earlier known interferences, although many new interferences were also found. The calculated interference magnitudes for highly ionizable elements merely followed the earlier observations by Blades and Horlick. Thus our combined interference element study is of practical value and can be used instead of time-consuming single element studies. The effect of the combined elements on the element under analysis may strengthen or weaken or compensate for each other. Where interfering elements are included in the sample matrix, single element interference studies can give rise to erroneous conclusions.

In this study the best analytical wavelengths of five fertilizer elements for ICP-AES determination were 208.959 nm for boron, 383.826 nm for magnesium, 238.204 nm for iron, 180.731 nm for sulfur and 396.847 nm for calcium. The selection of wavelength was made according to both the calibration data and the interference studies.

The main aim of developing new standard methods for the determination of fertilizer minor elements by ICP-AES was achieved. Three new SFS standards have been accepted by the Chemical Industry Federation of Finland. These standards are "Nitrogen Rich Fertilizers - Determination of Water-Soluble Boron by ICP", "Nitrogen Rich Fertilizers - Determination of Water-Soluble Magnesium by ICP" and "Nitrogen Rich Fertilizers - Determination of Acid-Soluble Magnesium by ICP". On the basis of our studies it is also possible to write outlines for SFS standards for AS boron, WS and AS sulfur and AS iron determination from nitrogen rich fertilizers by ICP-AES.

Because ICP-AES is suitable for multielement analysis, further work should be directed towards the determination all the relevant fertilizer elements from the same sample solution with as high a level of accuracy as possible. The procedure described in this study is applicable to other sample matrices and it is more easy to perform than a single element interference study. Critical basic research should be done in the case of every sample matrix for which interferences can be minimized.

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PAPER I

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