ICP determination of phosphorous in soils and plants

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Abstract

The purpose of our study is to evaluate the appropriateness of an ICP–method for the determination of total phosphorus content in soils and plants after complete decomposition by acid mixtures. Three certified soil samples corresponding to two main soil types in Bulgaria and Polish reference material CTA-VTL-2 (Virginia tobacco leaves) were used in the study. It was established that ICP is a fast and correct method for phosphorus determination in plant materials. We have to use a standard supplement method in order to obtain correct results for soil samples.

Key Words

Phosphorous determination, ICP, soils, plants

Introduction

The correct determination of phosphorus content in soils and plants is extremely important for agricultural science and practice. Phosphorus participates in a number of processes determining the growth, development and the productivity of the plant: formation of cell nucleus and cell multiplication, synthesis of lipids and specific proteins, transmission of hereditary properties, breathing and photosynthesis, energy transmission from richer to poorer energetic compounds, etc. It is very important to know the phosphorus status of soils to determine the necessity for phosphorus fertilizer use. Phosphorus is known to be unique for its sensitivity and stability as a human activity indicator. Its content in soil represents a great interest to archaeologists, giving them information on type and intensity of human activity. Total phosphorus measurement gives quantitative results in contrast to mobile phosphorus and represents the best indicator for variation caused by human activity.

During the last year soil and plant laboratories have moved from colorimetry to inductively coupled plasma (ICP) spectrometry to quantify phosphorous in soil and plants (Sicoria et al. 2005). The main reason is the increasing critical attitude to the colorimetric measurement due to the significant interference problems upon P determination in soils and plants, as well as the advantages of ICP–method related to the fast measurement and the opportunity to simultaneously determine the main part of the macro-and microelements, contained in soils and plants. Its adaptation and priority for soil status evaluation is not trouble-free due to controversial results when compared to the colorimetric method. We have expanded the studies in this sphere to obtain more experimental results related to sample preparation methods and soil diversity. Several profound studies comparing both methods for determination of total and mobile phosphorus in various soils are known. Upon the test falling within the scope of North American Proficiency Testing (NAPT) program conducted in 2001 and 2002, 18 laboratories used the spectrophotometric method and 34 laboratories used the ICP–method (Sicoria et al. 2005). In 40 samples ICP values for phosphorus, extracted by Mehlih 3 (Mehlih 1984) exceeded the values determined by means of spectrophotometric method by 7.4 mg/kg on average. Thus the ICP–method is not recommended for determination of standards for phosphorus fertilizers. Pitman et al. (2005) compared phosphorus determined by ICP and spectrophotometric methods in Mehlich 3 extract of 6400 soil samples and established a significant correlation between both methods at P concentrations exceeding 60 mg/kg, the P determined by the spectrophotometric method was 80–90% of the phosphorus determined by ICP–method. Sicoria et al. (2005) studied 1536 soils having various origins and found significant differences between both methods. Values obtained by ICP are higher in most cases, but a few samples showed the opposite result. According to Piersynski et al. (2005) the ICP results for phosphorus contained in aqueous extracts of fertilizers were up to 15 % lower than those determined by the spectrophotometric method. The reasons for these results are not clarified yet.

A summary of the results published in the scientific literature showed that the ICP–method gave higher results for total phosphorus content in soils in comparison to the spectrophotometric method. However, the exceptions and controversial results are significant, so that we may not come to an explicit conclusion. We must bear in mind that hydrofluoric acid was not used for dissolution of the analysed samples in any of the

studies, i.e. the soil silicate matrix did not enter solution. It is necessary to simultaneously determine the total content of phosphorus and of the other macro-and microelements for the purpose of numerous studies. The purpose of our study is to evaluate ICP–method appropriateness upon solving the present problem.

Materials and methods
Type of samples
Three certified soil samples corresponding to two main soil types in Bulgaria were used: (i) Light Alluvial-deluvial Meadow Soil PS-1, SOOMET № 0001 – 1999 BG, SOD № 310[a]-98; (ii) Light Meadow Cinnamonic Soil PS-2, SOOMET № 0002 - 1999 BG, SOD №311[a]-98 and (iii) Light Alluvial-deluvial Meadow Soil PS-3, SOOMET № 0003 - 1999 BG, SOD № 312[a]-98. The total content of phosphorous in the certified samples is presented in Table 1.

Table 1. Phosphorous content in the certified soil samples. X_{CRM} is the certified value, U_{CRM}, % - the uncertainty of the certified value and σ_{CRM} - the standard deviation from of the certified value.

Soil	$X_{CRM},$ %	$U_{CRM},$ %	$\sigma_{CRM,}$ %
PS-1	0.197	0.014	0.003
PS-2	0.150	0.010	0.006
PS-3	0.205	0.013	0.007

A Polish reference material CTA-VTL-2 (Virginia tobacco leaves), containing 2204 ± 78 µg/mg phosphorous was used in the study.

Digestion method
A main consideration in the selection of digestion methods was the possibility for simultaneous determination of the most important macro- and micronutrients in the soils and plants by a single digestion procedure. Our preliminary studies showed that the most appropriate digestion methods are ISO 14869-1 (2001) (decomposition by acid mixture of $HF + HNO_3 + HClO_4$) for soil samples and EPA METHOD 3051(decomposition by acid mixture of $HNO_3 + H_2O_2 + HF$) and dry ashing at 500^oC for plant materials.

Phosphorus determination
An ICP-AES spectrometer Spectroflame MODULA (Spectro Analytical Instruments, Kleve, Germany), equipped with two monohromators: (i) spectral range 160 – 460 nm with nitrogen purged optics and (ii) spectral range 240 – 790 nm with air purged optics, was used. Background correction was performed. We used the internal standard method by adding scandium to the samples and standard solutions. The calibration was performed using three standard solutions in 2 % v/v HNO_3. A commercial multielement standard solution with concentration 100 µg/l was used as a stock solution. The calibration standard solutions had the following concentrations: 0,0; 5.0 and 10.0 ppm.
With the aim to define the magnitude of the difference between ICP and colorimetric P in the soils and plant material investigated, we analysed the same solutions, obtained by the digestion methods described above, following the colorimetric procedure for P determination, described by Gorbanov *et al*. (1990)

Statistical analysis
For evaluation of the correctness of the results for phosphorous three generally accepted criteria were used as follows: (i) $D = X – X_{CRM}$, where X is the measured value and X_{CRM} is the certified value. When D is within the limits of $\pm 2\sigma$, where σ is the standard deviation from the certified value, the result is considered to be good; when it is $-3\sigma \leq D \leq 3\sigma$ - satisfactory, and beyond these limits the result is unsatisfactory ; (ii) $D \% = D/ X_{CRM} .100$ – percentage difference. When the values of D % are in the limits $\pm 200\sigma / X_{CRM}$ the result is considered to be good, when the value is within the limits $\pm 200\sigma/ X_{CRM}$ and $\pm 300\sigma/ X_{CRM}$ - satisfactory, and when it is out of the limits $\pm 300\sigma/X_{CRM}$ the result is unsatisfactory; (iii) $Z = X – X_{CRM} / \sigma$. When $Z \leq 2$ the result is considered to be good, when $2 \leq Z \leq 3$ - satisfactory, when $Z > 3$ - unsatisfactory. We have used the R criterion showing the extent of extraction of the element in percents from the certified value. When the measured value X is within the borders of $X_{CRM} \pm U_{CRM}$ where U_{CRM} is the indefiniteness of the certified value, we accept the extent of extraction to be 100%. In all remaining cases the extent of extraction is equal to $X/X_{CRM}.100$.

Results

Soil samples

The results obtained by ICP and colorimetric analyses of phosphorous in soil samples are presented in Table 2.

Table2. Effectiveness of ICP and colorimetric determination of phosphorous in soil samples.

Soil	X, %	U_x, %	σ_x, %	D	D, %	Z	R
PS-1, ICP	0.156	0.010	0.001	-0.041	-20.81	-18.33	79.19
PS-1, Colorimetric	0.206	0.014	0.003	0.009*	4.57*	3.00*	100
PS-2, ICP	0.121	0.006	0.001	-0.029	-19.33	-10.50	80.67
PS-2, Colorimetric	0.151	0.011	0.007	0.001**	0.67**	0.17**	100
PS-3, ICP	0.159	0.010	0.001	-0.046	-22.4	-22.67	63.60
PS-3, Colorimetric	0.202	0.014	0.006	-0.003**	-1.46**	-1.00**	98.5

* - "satisfactory" results; ** - "good" results

As seen from the results, presented in the table 2, all values related to the phosphorus content, determined by ICP, are significantly lower. This contradicts most of the results published in scientific literature. It is well known that the *calibration line method (CLM)* is the most commonly used method for quantitative measurements by ICP. It is constructed according to standard solutions prepared by appropriate dilution of mono- or multi-standard with one or two percent solution of the respective acid used for sample mineralization. Some multiplicative interferences resulting from the matrix may be compensated by the *standard supplement method (SSM)*. For that purpose two or three supplements of the standard solution shall be added to aliquot parts of the analyzed sample at concentrations which are close to the supposed concentration of the element in the sample. A supplement shall not be added to one of the aliquot parts. The intensity of samples with or without supplements shall be taken into account and the obtained points shall be used for first degree polynomial calculation by the method of the smallest radicals. The point where this line crosses the horizontal coordinate C_{SSM} according to the module corresponds to element concentration in the sample calculated by the standard supplement method. In case of matrix interferences the line according to the standard supplement method has smaller declination than the calibration line and, respectively, C_{SSM} is greater than C_{KLM}. Four points are used for calibration line construction – one empty sample and three having concentrations of 4,0 8,0 and 12,0 mg/l. Three points were used for each of the studied samples - one without supplement and the other two with supplements of 4,0 and 8,0 mg/l, respectively, for construction of the line according to the standard supplement method. Mathematical statistics for checking the hypothesis related to the parallelism of two regression equations was used for checking the parallelism of the constructed lines. Fig. 1 demonstrates phosphorous determination by SSM method on the base of PS-3 sample.
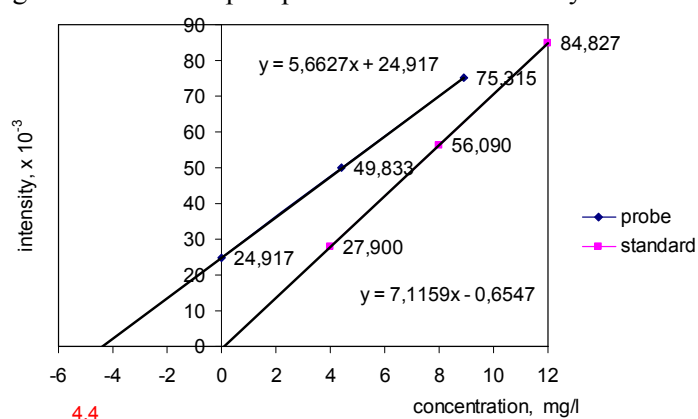

Figure 1. Phosphorous determination in PS-1 by standard supplement method (SSM).

The results obtained for all certified samples are presented in Table 3.

Table 3. Phosphorus content in certified samples determined by CLM and SSM. C_{CLM} – solution concentration by CLM; C_{SSM} - solution concentration by SSM; $C_{P.\,CLM}$ % – P content by CLM; $C_{P.SSM}$ % - P content by SSM; ▲ - difference between both methods in %.

Soil	$X_{CRM,}$ %	C_{CLM}	$C_{P.\,CLM,}$ %	C_{SSM}	$C_{P.SSM,}$ %	▲, %
ПС-1	0.197	3.4	0.156	4.2	0.192	23.0
ПС-2	0.150	2.6	0.120	3.2	0.147	22.5
ПС-3	0.205	3.4	0.156	4.4	0.202	29.5

As seen from the data, presented in table 3 the phosphorus content determined by the standard supplement method in the three samples significantly exceeds the phosphorus content determined by the calibration line method, and the extraction degree is 100 % in all three cases. Although the matrix interference for all three studied samples was close, the introduction of a common correction factor for the results obtained by the calibration line method required accumulation of more experimental results and their mathematical processing.

Plant materials
The results obtained for CTA-VTL-2 (Virginia tobacco leaves), digested by EPA method 3052 and dry ashing are presented in Table 4.

Table 4. Effectiveness of ICP and colorimetric determination of phosphorous content in tobacco leaves. X_{CRM} = 2204 ppm, σ_{CRM} = 78 ppm.

Method	X, ppm	σ_x, ppm	D	D, %	Z	R
Dry ashing, ICP	2430	220	226*	10,25*	2,90*	100
Dry ashing, colorimetric	2260	112	56**	2.54**	0.72**	100
EPA method 3052, ICP	2355	110	151**	7.08**	2.00**	100
EPA method 3052, colorimetric	2430	95	226*	10.25*	2.90*	100

* - "satisfactory" results; ** - "good" results

As seen from the data colorimetric and ICP methods for total phosphorus determination are highly correlated and the results are generally within 5 to 10 % of each other.

Conclusion
The results of the determination of total phosphorus in soils by ICP after complete sample dissolution by HF showed that the calibration line method provided lower values. That is why simultaneous determination of P with other macro- and microelements is risky. In all cases we have to use standard supplement method in order to obtain correct results. In the case of plant materials phosphorous content can be determined directly by the calibration line method.

Acknowledgement

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