DETERMINATION OF BIOGENIC ELEMENTS
IN A PLANT MATERIAL BY X-RAY SPECTROSCOPY. I.
MACROELEMENTS

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A quantitative X-ray spectroscopic method for the determination of potassium, calcium, sulphur, phosphorus in cereals was developed. The original material is pulverised without any further chemical treatment. An accuracy of 0·7—1·8 rel.% was achieved. The X-ray determination agrees with the chemical analysis within 3—4 rel.%. Time requirements of the new method are 15—20 minutes per analysis.

The study of the plants capability to accept the biogenic elements added into the soil in fertilizers and the mechanism of this process are the main tasks of the agrochemical research. Large number of samples must be analysed owing to the large number of factors influencing this process. The authors tried to substitute the so far used chemical means of analysis, whose time consumption is mainly caused by the necessary sample decomposition, by a non-destructive X-ray spectroscopic analysis. According to the common agrochemical practice the work was divided in two parts: the determination of macroelements and the determination of microelements.

The analytic procedures and their results in the determination of macroelements potassium, calcium, sulphur, and phosphorus are reported in the presented paper; the present stage of the X-ray spectroscopy instrumentation does not allow the determination of nitrogen. There are only few articles in the literature dealing with this subject[1-3].

EXPERIMENTAL

Sample and its preparation for analysis. Four sorts of cereals (wheat, rye, barley, and oats) in various growth stage (from early growth to grain and straw) were examined; 18 kinds of material were analysed. The individual samples were perfectly homogenized, ground and pressed under the pressure of 2·5 t/cm² in pellets of 32 mm diameter and 2 g weight. The pellets were introduced into the measuring cells without Mylar foil. This procedure was chosen for its speed and simplicity; other procedures converting the sample into ash or using its mineralization are less suitable for the routine measurement owing to the greater time consumption.

Apparatus and measurement. A Philips PW 1540 vacuum X-ray spectrograph was used (1 kW high voltage source, X-ray source with Cr anticathode, gypsum crystal $-2d = 15·185$ Å, the detection of the secondary X-radiation by a proportional flow counter filled by argon–methane mixture connected with an amplitude analyser, 480 µm Soller slits). All measurements were

carried out *in vacuo*. The method of time preselection was applied for the measurements of the analytical lines of the analysed elements. Three pellets were prepared from each sample and each pellet was measured three times for 32 s. Following quantities were measured: the intensity of the analytical line (L) including background, the intensity of the background in its vicinity (L^0), the intensity of the Cr $K_{\alpha_{1,2}}$ line of the source diffracted by the sample (L_{Cr}), and its background (L^0_{Cr}). The Cr line measurement was used as an internal standard according to Andermann[4] in order to eliminate an eventual effect of the sample matrix variability in different materials. All measurements were corrected using an external standard to suppress the long-term changes in the apparatus.

Evaluation. The method of calibration curve based on the results of chemical analysis was used for the evaluation of the cereals analyses. This method was chosen because of difficulties in the application of direct methods (the method of standard increments, the method of artificial standards) due to the character and the matrix complexity of the studied material. The calculations of the calibration curves were performed using the least-squares method for nine alternatives of the measurement including the variation of the number of pellets prepared from one sample, the effect of neglecting the analytical line background, chromium line background, and the significance of the Andermann's correction. The recommended alternative for given element was selected with respect to the required accuracy and minimum time consumption and is given in the part Results and Discussion. Under the term "accuracy of the determination" is understood the percentual mean deviation $\bar{\sigma}$ in this paper.

Methods of chemical analysis used for comparison. The plant material was decomposed by sulphuric and nitric acid. The elements were then determined in the solution obtained after mineralization: potassium by flame photometry, calcium by chelatometric microtitration, and phosphorus colorimetrically by ammonium molybdenate (after reduction). Sample combustion in the oxygen atmosphere was used in the sulphur determination. Sulphur was determined by weighing as $BaSO_4$. The results of chemical analyses used to the construction of the calibration curves were means of five parallel determinations (two in the case of sulphur). The achieved accuracy of chemical analysis was ($\bar{\sigma}$ values): 1·2, 3·5, 1·0, and 2·1 rel. % for K, Ca, S, and P, respectively.

RESULTS AND DISCUSSION

Determination of Potassium

The determination of potassium was based on its most intense line $K_{\alpha_{1,2}}$ I. The calibration curve was derived for a mean value taken from the measurements of three pellets per sample with introduction of the Andermann's correction and the correction on the background. It is expressed by equation

$$y = -0.243 + 1.406\, x. \qquad (1)$$

The accuracy of the X-ray spectroscopic determination $\bar{\sigma}$ is ± 0.7 rel.%; the agreement with chemical analysis $\bar{\Delta}$ is 0·11 abs.%. From the calibration curve and from the results it follows that potassium can be determined quantitatively in the range $0.4 - 6.0\%$ K_2O using only one universal calibration curve for the all 18 analysed samples of cereals.

By examination of the various alternatives of the measurement it was found that neither the omission of the measurement of the background nor the reduction of the

number of pellets to two or one, had any substantial effect on the results of potassium determination. However, a fundamental meaning has the introduction of the Andermann's correction. Without it the mean deviation rises to $\bar{\sigma} = \pm 1.02$ rel.%, $\bar{\Delta}$ changes to $\bar{\Delta} = 0.14$ absolute %, and the calibration curve becomes an exponential $y = a \cdot e^x$ instead of straight line.

The optimal conditions for routine potassium determination appear to be the measurement of two pellets, neglecting the background of both lines, and the application of the Andermann's correction. One analysis lasts about 15 minutes in this arrangement.

Determination of Calcium

The calcium $K_{\beta_{1,3}}$ I spectral line was chosen for the purpose of the quantitative determination. The most intense $K_{\alpha_{1,2}}$ I calcium line could not be used because of its partial coincidence with the potassium $K_{\beta_{1,3}}$ I line. The calibration curve measured under the same conditions as for potassium follows the equation

$$y = -0.008 + 0.945x . \tag{2}$$

The agreement between the results of X-ray spectroscopy and chemical analysis is $\bar{\Delta} = 0.01$ abs. %, the accuracy of the former method $\bar{\sigma}$ is ± 1.2 rel.%. The examination of various measurement arrangements shows that for routine analysis the number of determinations can be reduced to two measurements without substantial changes in $\bar{\sigma}$ but the measurement of L_{Ca}^0 cannot be (in contrary to potassium) neglected. Important is also the Andermann's correction; without it the $\bar{\Delta}$ value increases to 0.03 abs.%. Again the same calibration curve can be used for all kinds of the analysed material $(0.05-0.70\% \text{ CaO})$. The analysis of one sample takes about 20 minutes.

Determination of Sulphur

The most intense $K_{\alpha_{1,2}}$ I sulphur line was used for the analysis. The calibration curve constructed for the alternative $(L_S - L_S^0)$ is expressed by equation

$$y = 0.013 + 0.506x . \tag{3}$$

Only the correction on the analytical line background was considered. The Andermann's correction has no effect in this case — in contrary to potassium and calcium. The reason is probably the large difference between the sulphur and chromium wavelengths $\left(\lambda \, SK_{\alpha_1} = 5.361 \, \text{Å}, \, \lambda \, CrK_{\alpha_1} = 2.285 \, \text{Å}\right)$ so that the chromium wavelength does not fulfil the requirements of an internal standard with respect to sulphur. An attempt to use the background of the analytical line as an internal standard did not bring any improvement of the results. The accuracy of the method is $\bar{\sigma} = \pm 1.8$ rel.%. A comparison of the X-ray spectroscopic and chemical analysis

determinations leads to the mean difference $\overline{\Delta} = 0.007$ abs. % for the sulphur content $0.118 - 0.462\%$. The number of measured pellets can be reduced (similarly to the above described cases) to two pellets without substantial changes in the accuracy. Analysis of one sample takes about 15 minutes.

Determination of Phosphorus

The most intense phosphorus $K_{\alpha_{1,2}}$ I line was employed to the X-ray spectroscopic determination. However, this line is partially overlapped by the calcium $K_{\beta_{1,3}}$ II line. Owing to the remarkable difference between the wavelengths of both lines the interfering effect of calcium in the phosphorus determination can be eliminated by amplitude analysis.

The calibration curve was obtained in the same manner as for sulphur, i.e. $(L_P - L_P^0)$. Its equation is

$$y = 0.00066 + 0.354x . \tag{4}$$

A comparison of the X-ray spectroscopic phosphorus determination with chemical analysis leads to the $\overline{\Delta}$ value equal to 0.022 abs.%. The accuracy of the determination $\overline{\sigma}$ is ± 1.5 rel.%. The analysis of one sample takes about 15 minutes. The determination of the phosphorus content in cereals is the only case where one calibration curve for the all sorts of cereals and for all growth stages is not sufficient; the exception is the analysis of grain. It was found by chemical analysis that the phosphorus distribution in the grain is not uniform, the main part being concentrated in the peel. Since the weight portion of the peel in the sample is small and its particles are always greater than that from the other parts (the flour), a certain part of the peel can be blocked by powdering by the flour during the sample elaboration. This resulted in determining lower contents of phosphorus which fact was proved experimentally. Therefore it is necessary to construct an extra calibration curve for the analysis of grain.

REFERENCES

1. Ball D. F., Perkins D. F.: Nature *194*, 1163 (1962).
2. Champion K. P., Whittem R. N.: Analyst *93*, 550 (1968).
3. Jenkins R., Hurley P. W.: Analyst *91*, 395 (1965).
4. Andermann G., Kemp J. W.: Anal. Chem. *30*, 1306 (1958).