X-RAY SPECTROCHEMICAL DETERMINATION OF POTASSIUM IN CLAY MINERALS*

LEON J. JOHNSON

Department of Agronomy, The Pennsylvania State University, University Park, Pa. 16802

Abstract – An X-ray spectrochemical method is compared with the flame photometer determination of potassium in a series of sixty-five soil clay fractions. Two methods of preparing the clay samples for the X-ray determination were used. In one case a 20 mg sample of clay in suspension was dried onto a plastic disc as a thin film. Potassium was determined by comparing the fluorescence intensity of the unknown with a sample of known composition which was prepared for analysis by the same technique. For the second method a 100 mg sample of dried clay was pressed into a pellet using methyl cellulose as a backing. In this case a National Bureau of Standards sample (NBS-98) was prepared in an identical manner and used as a standard for determining the potassium in the unknown. The results for both techniques were highly significantly correlated with the values as determined by flame photometric analysis. The pellet technique gave a more accurate measure of the potassium content. With the thin films the same sample may be used for X-ray diffraction analysis. In either case the X-ray spectrochemical technique provides a fairly rapid and simple procedure that can be useful for handling large numbers of samples.

INTRODUCTION

RESEARCH in soil science and clay mineralogy requires quantitative analysis of potassium in clay separates. A relatively rapid simple procedure for this analysis would be of much value, particularly when a large number of samples is to be analyzed. A technique that appears amenable to this goal is X-ray spectrochemical analysis. In the research reported below two methods of sample preparation, pressed pellets and thin films, were tested and the results are compared to potassium determined by flame photometry after hydrofluoric acid dissolution.

MATERIALS AND METHODS

Sample description

All the clay separates used were obtained from samples of Pennsylvania soils collected either by the Soil Characterization Laboratory (Dr. R. P. Matelski in charge) at The Pennsylvania State University in cooperation with the Soil Conservation Service (J. Noll and F. G. Loughry, present and former State Soil Scientist respectively) or by the author. Detailed descriptions of all the soils used are irrelevant for this report and are not included. However, in the course of the research several of the soil clay separates

were selected as standards to represent a range in content of potassium and other elements. The source of these samples and some pertinent chemical and mineralogical data are listed in Tables 1 and 2. In addition to these soil clay separates use was made of the National Bureau of Standards samples NBS-98 and NBS-78 in experiments with the pressed pellet technique.

Sample preparation

The $< 2\,\mu$ clay fraction was separated from the soils by centrifugation after removal of organic matter by H_2O_2 and dispersing the soil according to methods described by Jackson (1956, pp. 31–171). Free iron oxides were removed either by the nascent hydrogen method of Jeffries (1947) or by the dithioninte-citrate technique of Mehra and Jackson (1960). For the great majority of samples analyses were made without prior removal of free iron oxides.

Exchange sites on the clays were saturated with either magnesium or hydrogen for several reasons. Removal of any salts present by washing with water is facilitated because these ions maintain the clay particles in a flocculated condition. A flocculated state is also desirable when preparing thin films because it would tend to limit differential settling and the consequent non-uniformity in composition perpendicular to the film surface. Any non-uniformity of this nature would reduce the precision and accuracy of the potassium

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Table 1. Source and composition of soil clays used as standards

Soil series	Location in Pa.	Lab. No.*	Horizon	Clay† minerals	%K_2O
Ashby	Huntingdon Co.	---	C	$\underline{I}, C-V$	4·8, (5·1)‡
Hublersburg	Centre Co.	14–6–8	C_1	$\underline{K}, I, V-C$	1·0, (1·2)‡
De kalb	Clinton Co.	18–4–3	A_2	$\underline{C-V}, K, I$	1·6
Cavode	Indiana Co.	32–52–6	C_2	$\underline{I-M}, K$	4·9
Mount Lucas	Adams Co.	1–16–4	B_{22g}	$\underline{M}, K, I$	0·7
Watchung	Adams Co.	---	B_3	M, K, I	0·7
Edom	Centre Co.	14–1–4	C_2	$\underline{I-M}, C$	5·0
Allenwood (1–2)	Mifflin Co.	---	A_2	$\underline{C-V}, K, I$	1·7
Allenwood (1–4)	Mifflin Co.	---	C	$\underline{V}, K, I$	2·8
Hagerstown (2810)	Centre Co.	---	C	$K, I, C-V, M$	1·7

*Soil Characterization Laboratory, The Pennsylvania State University.
†C-chlorite, I-illite, K-Kaolinite, M-montmorillonite, V-vermiculite. A dash between a pair of letters indicates interstratification. The major component is underlined.
‡K_2O content after free iron oxide removal.

Table 2. Range of composition of the standard soil clays

	(%)
SiO_2	40·5–55·6
Al_2O_3	22·3–34·8
Fe_2O_3	1·06–12·1
TiO_2	0·02–1·04
K_2O	0·72–5·10
H_2O^+	0·23–15·41

determination by X-rays due to absorption effects. In addition, these ions would not be expected to be a source of interference either by absorption or enhancement of potassium K-alpha radiation.

Thin film preparation. As a backing for the thin films it was desired to have a smooth, rigid material that would not produce interfering X-radiation. On this basis it was decided to use plastic. The sample holders on the equipment used require a circular mount 1·25 in. in diameter. Discs of this size were cut from 1/8" or 1/16" thick plexiglass. The extreme smoothness of this material resulted in the peeling of many samples from the surface upon drying. This difficulty was circumvented in most cases by frosting the surface of the discs by grinding briefly with a fine carborundum grit.

Samples were then mounted by pipetting the requisite amount of clay suspension onto the discs and drying at room temperature. After some experimentation it was decided that a 20 or 40 mg sample was satisfactory. Four discs were prepared for each sample analyzed.

Pressed pellet preparation. Clay which had previously been saturated with magnesium or hydrogen was washed twice with ethyl alcohol and acetone, dried at room temperature, then oven dried at 105–110°C overnight and stored in a dessicator. With a die, (Baird, 1961) pellets were pressed at 10,000–12,000 lbs/in² using 100 mgs of sample and methyl cellulose as a backing. For a uniformity test four pellets per sample were employed whereas in the other analyses two pellets per sample were used.

Chemical methods

Samples for flame photometric analyses of potassium were treated by the procedure of Shapiro and Brannock (1956). The potassium was determined with either a Perkin Elmer Model 52-C or a Beckman DU flame photometer.

Instrumentation

X-ray spectrochemical analyses were made with a Norelco Universal Vacuum X-ray spectrograph. Instrumental settings used for the potassium analysis are listed in Table 3. The pulse height analyzer was recalibrated each day according to a procedure outlined in the manufacturer's instrument manual. To counteract the effect of instrumental drift on the intensity data a standard sample was run before and after an unknown. The average of the two values was then used to calculate the potassium content of the unknown according to the following equation:

$$\text{per cent } K_2O \text{ (unknown)} =$$

$$\text{per cent } K_2O \text{ (standard)} \times \frac{c/p \text{ (unknown)}}{c/p \text{ (standard)}} \quad (1)$$

Table 3. X-ray spectrographic instrument settings

X-ray tube-	Tungsten target
	50 KV
	45 ma
Analyzing crystal-	EDDT
Radiation counter-	Gas-flow proportional
Pulse height analyzer-	22·5 V level
	21·0 V width
Other-	Fixed time – 20 sec
	Time constant – 0·5 sec

RESULTS AND DISCUSSION

Thin film technique

*Uniformity test** When the work on this problem was initiated it appeared desirable to obtain a measure of the minimum difference in potassium content detectable by the experimental set up used. Accordingly a uniformity test was undertaken to measure the contribution to variance of the major variables involved in the analyses. The variables included thin film replications, sample holders on the instrument, and their interaction. Quadruplicate intensity measurements on a single thin film within a sample holder was used as a measure of error. Four thin films (discs) were prepared for each of five standard soil clays using a 20 mg sample per disc. For two of the standards 40 mg samples were used. Intensity measurements were made for every disc in each of the four sample holders on the instrument. Within each holder four intensity measurements of 20 sec duration were taken. In toto, sixteen measurements were made on each disc and sixty-four measurements on each standard soil clay used.

*Dr. J. L. Starling provided helpful counsel on the statistical methods and interpretation.

An analysis of variance indicated that variation among discs within a sample was the principal contributor to variance in the majority of cases. Using the mean square among sample discs as a measure of error, computations were made of the minimum significantly different (95 per cent probability level) potassium content detectable as a function of the number of discs prepared for a sample. In Table 4 these minimum differences are expressed as a percentage of the mean. The resulting values are a measure of the precision of the technique. Thus if only one disc is used the error, averaged over the five soil clays, is ±8·4 per cent of the value measured. With four discs this is halved to 4·2 per cent. It may be emphasized that the data used to arrive at these values of precision are the most conservative possible. When the pooled variation of discs, holders, and the interaction is used as the error mean square the resulting precision is 5·0 per cent and 2·5 per cent for one and four discs respectively. It was decided that the most efficient procedure, without significantly sacrificing any precision, was to prepare four discs and to take one intensity reading on each disc in one of the sample holders, giving a total of four readings on one sample.

Film thickness. The thickness of the clay film deposited on a disc can have considerable influence on the magnitude of the fluorescence intensity and the variation among replication of a sample. This is a result of the nature of the process involved. X-rays entering and emerging from a sample are subject to absorption the extent of which is a function of film thickness and composition. This relationship is summarized in an equation (Liebhofsky *et al.*, 1960, Eq. 6–8, 154):

$$Id/I^\infty = 1 - e^{-apd} \qquad (2)$$

Table 4. Precision of the potassium determination as a function of the number of
THIN FILMS

Clay source	Ashby	Ashby	Cavode	Cavode	Allenwood (1–4)	DeKalb	Hublersburg	
Sample weight (mg)	20	40	20	20	20	20	20	
K_2O (%)	5·1	5·1	5·2	5·2	2·8	1·6	1·2	
No. of discs	Precision ($2s\bar{x}d^*/\bar{x} \times 100$) (%)							Average
1	11·1	7·2	8·1	9·1	4·5	5·6	12·8	8·4
2	7·8	5·1	5·7	6·5	3·2	4·0	9·0	5·9
3	6·4	4·2	4·7	5·3	2·6	3·2	7·3	4·8
4	5·5	3·6	4·0	4·6	2·3	2·8	6·4	4·2

*Standard error of mean difference

where the symbols are defined as:

Id intensity at thickness d
I^∞ intensity at infinite thickness
a an absorption factor involving the mass absorption coefficient of the sample for the incident and fluorescent radiation and the angles between the sample surface and the incident and fluorescent radiation-$\mu_1 \csc \theta_1 + \mu_2 \csc \theta_2$
p the density of the sample
d the thickness of the film

From this equation it is seen that as $d \rightarrow \infty$, $e^{-apd} \rightarrow 0$ and $Id \rightarrow I_\infty$. At some critical value of the thickness the intensity, for all practical purposes, reaches a maximum and is then independent of the thickness. This relationship was investigated be preparing a series of discs using four of the standard soil clays and containing 5, 10, 20, 40 and 80 mg of clay. Since the discs are of the same or very similar size the relative film thicknesses should be approx. $1:2:4:8:16$. The data obtained are plotted in Fig. 1. Maximum intensity has been attained for the Allenwood, DeKalb, and Hublersburg at about 40 mg. The Cavode is very near maximum at 80 mg. It would seem desirable then to use a sample size of at least 40 and preferably 80 mg as a lower limit to insure that maximim intensity is closely approached. Two factors militated against this selection. Difficulty was encountered in preparing samples of this size because of peeling of the film from the plastic disc. This is the reason no value is plotted at 80 mg for the DeKalb clay. Second is the manifestation of segregation effects with the larger sample size. This is

evident for the Allenwood clay where the 40 mg sample actually has a higher intensity than the 80 mg sample. A nonuniform distribution of potassium within the film is the probable cause. Soil clay, being mixtures of more than one clay mineral, can, by differential settling from suspension, become nonuniform in composition in a direction perpendicular to the film. If a greater concentration of potassium occurs in the lower layers a thicker film (within the region of infinite thickness) can produce a lower intensity than a thinner one. It was finally decided that a 20–40 mg sample size would be satisfactory. The counting rate is sufficiently high from this size sample to yield satisfactory sensitivity with samples of low potassium content. If samples are prepared with reasonable care the variation due to film thickness should be held to a minimum. Potassium analyses using 20 and 40 mg sample sizes were compared for two of the soil clays, Ashby and Cavode. As seen in Table 4, in one case, Ashby, the 40 mg size is somewhat better whereas for the Cavode the 20 mg sample was better so that, over all, there may be little to select between the 20 and 40 mg size. In all subsequent determinations a 20 mg sample was used.

Analyses of clay separates. The twelve soil clays listed in Table 1 were analyzed according to the procedure described. One of the samples, Allenwood (1–4), was used as a reference to compensate for instrumental drift. The resulting data are plotted in Fig. 2 in which are listed the regression equation and correlation coefficient. Over 99 per cent of the variation in counts per second (CPS) are associated with the variation in potassium content of the samples. The range in potassium content of these clays, 0·72–5·10 per cent
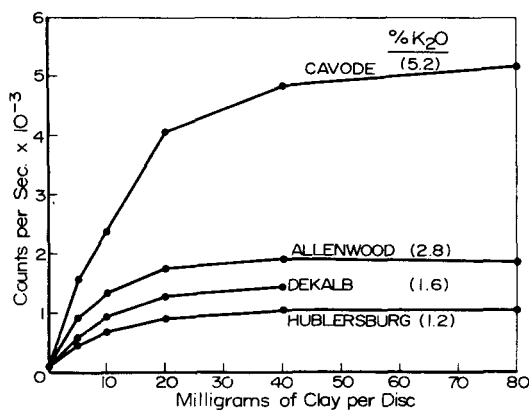

Fig. 1. Influence of film thickness on the intensity of potassium K-alpha radiation.
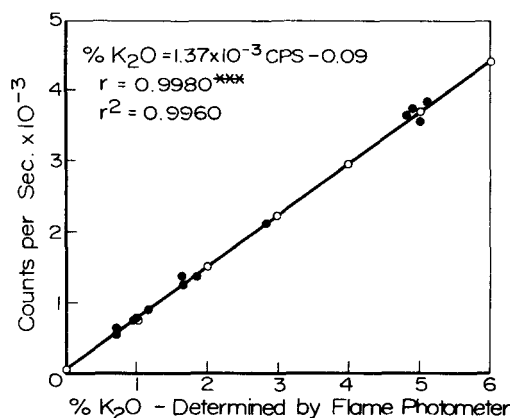

Fig. 2. Regression equation and correlation coefficient between potassium content and intensity of potassium K-alpha radiation for the standard soil clays. THIN FILMS.

K_2O, encompasses the amount that would be expected in most soil clay separates. Other elements present also cover a fairly large range in compostition (Table 2) without noticeably affecting the potassium determination. This would indicate that matrix effects are not serious.

In Fig. 3 data are plotted for a set of fifty-five soil clays available from a previous study and for which the potassium content had already been determined. These samples were originally hydrogen saturated and did not have the free iron oxide coatings removed. Correlation indicates that over 98 per cent of the variation in CPS is related to the flame photometer determined K_2O.

This same set of fifty-five soil clays was analyzed using two different soil clays, Cavode and Allenwood (1–4), as reference standards. The results obtained are presented in Fig. 4. It can be seen that very little difference exists between the K_2O values of the unknowns using either of these two soil clays as reference standards. With the high

degree of correlation found between intensity and percentage K_2O for the other standard soil clays, Fig. 2, it is concluded that any one of them could have been used with similar results expected.

Pellet technique

Uniformity test. The experiment previously described for the thin film samples was repeated using pressed pellets as the method of preparing the samples. Only two of the samples, Ashby and Allenwood (1–4), are the same as used in the thin film experiment and, in addition to soil clays, two National Bureau of Standard's samples, NBS-78 and -98, were used. Results are presented in Table 5. The precision is similar to that attained with thin films when equivalent samples are compared. On the basis of this experiment it was decided that for analyses of unknowns two pellets per sample would be satisfactory. Analyses would then be within approx. ± 5 per cent of the amount present. For the samples in the
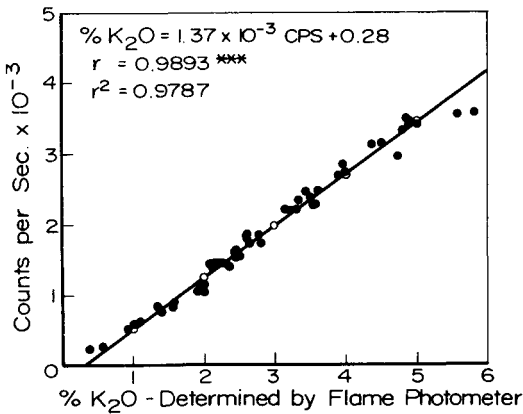

Fig. 3. Regression equation and correlation coefficient between potassium content and intensity of potassium K-alpha radiation for fifty-five soil clays. THIN FILMS.
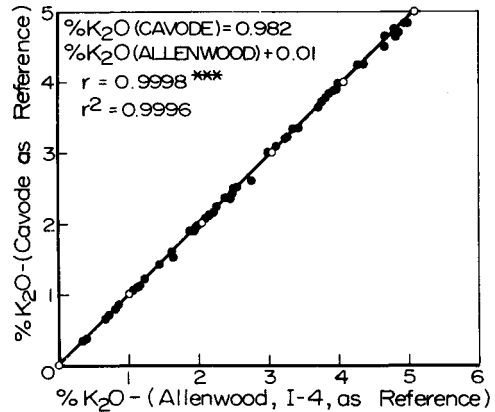

Fig. 4. Regression equation and correlation coefficient for the potassium determination using Cavode and Allenwood (1–4) as reference standards. THIN FILMS.

Table 5. Precision of the potassium determination as a function of the number of PELLETS

Clay source	Ashby	Edom	NBS-98	NBS-78	Allenwood (1–4)	Hagerstown	Allenwood	Hublersburg	
K_2O (%)	5·1	5·0	3·2	2·8	2·8	1·7	1·7	1·0	
No. of Pellets				Precision ($2S\bar{x}d/\bar{x} \times 100$) (%)					Average
1	5·1	7·3	2·8	4·7	5·2	2·8	5·8	9·2	5·4
2	3·6	5·1	2·0	3·3	3·6	2·0	4·7	6·7	3·9
3	2·9	4·2	1·6	2·8	3·0	1·6	4·1	5·3	3·2
4	2·5	3·7	1·4	2·3	2·6	1·4	3·3	4·9	2·8

uniformity test the range of precision for two pellets is 2·0–6·7 per cent with a mean of 3·9 per cent.

Analyses of clay separates. Analyses were made on the same samples previously described for the thin film technique. NBS-98 was the reference standard used. A separate intensity measurement was made on a pair of the standard pellets for each pair of unknown pellets analyzed Effects of instrumental drift were thus minimized. Results are summarized in Figs. 5 and 6 for the
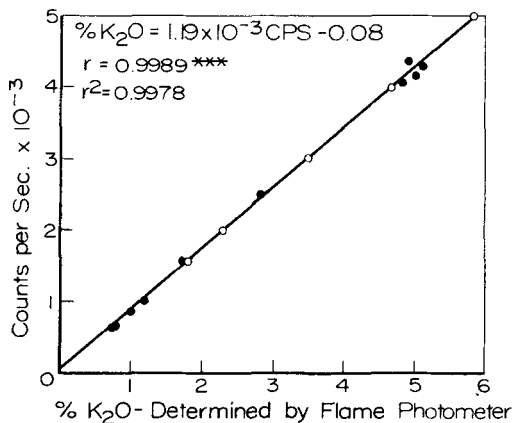

Fig. 5. Regression equation and correlation coefficient between potassium content and intensity of potassium K-alpha radiation for the standard soil clays. PELLETS.
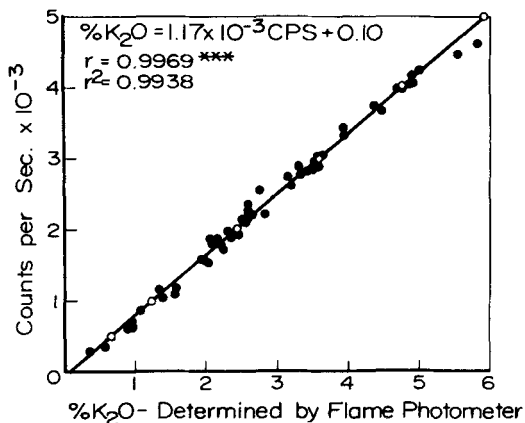

Fig. 6. Regression equation and correlation coefficient between potassium content and intensity of potassium K-alpha radiation for fifty-two soil clays. PELLETS.

twelve reference soil clays and fifty-two soil clays respectively. In both cases a very high degree of correlation was found between potassium fluorescent radiation intensity and per cent potassium as determined by flame photometry.

CONCLUSIONS

It is feasible with either technique described to determine potassium in a clay separate with a precision approaching ±5 per cent of the amount present. With the pellets duplicates are sufficient whereas the thin film technique would require a minimum of triplicates. The thin film method does have some ancillary advantages. An analysis could be done with a sample size as small as 100 mgs in contrast to the minimum of 200 mgs required by the pellet technique. Furthermore, the thin films may be used, without any additional treatment, for X-ray diffraction analyses of an oriented sample.

If the potassium content determined with a flame photometer is considered the standard for accuracy, the pellet technique is somewhat more accurate than the thin film, which is biased to low values. This is evident when the means over all samples for the flame, pellet, and thin film are compared −2·82, 2·81 and 2·62 per cent respectively. A segregation effect (higher concentration of potassium in the lower part of the film) is the probable explanation of this bias.

REFERENCES

Baird, A. K. (1961) *Norelco Reporter* **8**, 108–109.

Jackson, M. L. (1956) *Soil Chemical Analysis-Advanced Course:* Published by the author, Dept. Soils, Univ. Wisconsin, Madison 6, Wisconsin, pp. 31–101.

Jeffries, C. D. (1947) A rapid method for the removal of free iron oxides in soils prior to petrographic analysis: *Soil Sci. Soc. Am. Proc.* **11**, 211–212.

Liebhofsky, H. A., Pfeiffer, H. A., Winslow, E. H., and Zemany, P. D. (1960) *X-ray Absorption and Emission in Analytical Chemistry:* Wiley, New York.

Mehra, O. P., and Jackson, M. L. (1960) Iron oxide removal from soils and clays be a dithionite citrate system buffered with sodium bicarbonate: *Clays and Clay Minerals*, **7**, 317–327. [Pergamon Press].

Shapiro, L., and Brannock, W. W. (1956) Rapid analyses of silicate rocks: *Bull. Geol. Surv. U.S.* **103**–C.

Résumé – Une méthode spectrochimique par rayons X est comparée à la méthode par photomètre à flamme pour la détermination du potassium dans une série de soixante cinq calibrages d'argiles. Deux méthodes furent employées pour la préparation des échantillons d'argile pour la détermination par rayons X. Dans l'un des cas, un échantillon de 20 mg d'argile en suspension fut séché sur un disque en matière plastique sous forme de mince pellicule. On détermina le potassium en comparant l'intensité fluorescente de l'échantillon inconnu avec un échantillon à composition connue préparé pour l'analyse

selon la même technique. Pour la deuxième méthode, un échantillon de 100 mg d'argile séchés fut comprimé avec un support en méthylcellulose. L'échantillon (NBS-98) fut préparé de manière identique et servit de norme pour déterminer le potassium dans l'échantillon inconnu. Les résultats pour les deux techniques se trouvèrent, de manière très significative, en corrélation avec les valeurs telles qu'elles avaient été déterminées par l'analyse photométrique à flamme. La technique de l'échantillon comprimé donna une mesure plus exacte de la teneur en potassium. Avec les pellicules minces, le même échantillon peut servir pour l'analyse de diffraction par rayons X. Dans les deux cas, la technique spectrochimique à rayons X permet un procédé assez rapide et peu compliqué qui peut être utile pour la manutention d'un grand nombre d'échantillons.

Kurzreferat – Eine Röntgen-spektrochemische Methode wird verglichen mit der Bestimmung von Kalium durch das Flammenphotometer in einer Serie von fünfundsechzig Bodentonfraktionen. Zur Vorbereitung der Tonproben für die Röntgenbestimmung wurden zwei Methoden angewendet. In einen Fall wurde eine 20 mg Probe von suspendiertem Ton auf einer Kunststoffscheibe zu einem dünnen Film getrocknet. Das Kalium wurde bestimmt durch Vergleich der Fluoreszenzintensitat des unbekannten Materials mit einer Probe bekannter Zusammensetzung, die mittels der gleichen Technik für die Analyse vorbereitet worden war. Im zweiten Fall wurde eine 100 mg Probe von getrocknetem Ton unter Verwendung von Methylzellulose als Trägersubstanz zu einer Tablette gepresst. In diesem Fall wurde eine Probe in identischer Art nach dem Muster des National Bureau of Stanards (NBS-98) bereitet und als Vergleichsmittel für die Bestimmung von Kalium in der unbekannten Probe verwendet. Die Ergebnisse nach beiden Methoden ergaben eine sehr deutliche Korrelation mit den in der Flammenphotometrie erhaltenen Werte. Die Tablettenmethode ergab dabei ein genaueres Mass des Kaliumgehaltes. Im Fall des Dünnfilms kann die gleiche Probe auch für die Röntgenbeugungsanalyse verwendet werden. In beiden Fällen stellt die Röntgen-spektrochemische Analyse eine recht schnelle und einfache Methode dar, die bei Vorhandensein einer grösseren Anzahl von Proben nützlich sein dürfte.

Резюме—В докладе сравнивают рентгено—спектрохимический метод с пламенно—фотометрическим определением калия в серии 65 фракций почвенной глины. Применялисъ два способа приготовления образцов глины для рентгеновского определения. В одном случае высумили 20 мг пробы глины в суспензии и перенесли на пластмассовый писк в виде тонкой пленки. Калий определили сравнивая флуоресцентную интенсивностъ неизвъстного с образцом известного состава, приготовленного для анализа тем же способом. Во втором случае образец сухой глины весом 100 мг был вдавлен в гранулу, применяя метилцеллюлозу в качестве подкладки. В этом случае образец (американского) Националъного Ъюро Стандартов (NBS—98) был приготовлен тем же способом и применялся в качестве эталона для определения калия в неизвестном. Резулътаты обоих методов были оченъ значителъно коррелированы с величинами определенными пламенно-фотометрическим анализом. Метод полъзования гранулами дал более точный отсчет содержания калия. Пользуясъ тонкими пленками, тот же образец может быть применен в анализе рентгеновского излучения. В каждом из случаев, рентгено-спектрохимический метод предоставляет сравнителъно быстрый и простой метод, который может оказаться пригодным, когда имеется болъшое количество образцов.