

Determination of 16 Elements in Tobacco by Neutron Activation Analysis*

by A. Wytténbach, S. Bajo and A. Haekkinen

Institut Fédéral de Recherches en Matière de Réacteurs, Würenlingen, Switzerland

INTRODUCTION

Although there are several recent studies (1-3) on trace elements in tobacco by neutron activation analysis, it is difficult for the reader not familiar with activation analysis to grasp what this technique can do in helping him to establish analytical data for tobacco products, how fast he can get the results and what precision he can expect. The present communication concentrates on these methodological questions and the findings are exclusively restricted to analytical implications. The pertinent data have been obtained from a great number of analyses of different raw tobaccos and are thought to be representative. Elements determined by instrumental neutron activation analysis are Al, Ca, Mg, Cl, Mn, K, Na and Br, elements determined by neutron activation analysis with subsequent radiochemical separation Hg, Cu, Mo, Cd, As, Sb, Zn and Co.

GENERAL TECHNIQUES

The following section does not contain information on the general principles of activation analysis, which are amply covered by many textbooks. It is restricted to points that are specifically related to the neutron activation analysis of raw tobacco.

Sample Preparation

The raw tobacco was dried for 80 min at 105° C, which resulted in a weight loss of 10-15%. It was then ground and kept in air-tight bottles.

Sample Encapsulation

100 mg of the sample are encapsulated in containers of especially pure polyethylene. If Hg is to be determined the sample has to be encapsulated in quartz vials, since it is well known that the use of polyethylene containers results in low Hg values (4, 5).

Activation

For irradiations up to 30 minutes a pneumatic transfer-system with a time of transport of 6 seconds is used (6).

The irradiation position inside the reactor has a flux of $4 \cdot 10^{13} \text{ n/cm}^2 \text{ s}$ and a flux gradient of less than 1% over the volume of the transport container. It is thus possible to irradiate several samples and standards together under exactly the same conditions. Longer irradiations are made in a conventional irradiation position.

Sample Dissolution

For the determination of Hg, Cu, Mo, Cd, As, Sb, Zn and Co the sample has to be chemically processed, since the small activities resulting from these elements are completely masked by the much larger ^{24}Na -activity. Dissolution is done as follows: The irradiated quartz vial is cooled in liquid nitrogen and broken; 100 µg of each element are then added as carrier and the sample is gently heated with 10 ml concentrated HNO_3 and 5 ml HClO_4 (60%) in a beaker. The resulting solution is transferred into a 100 ml borosilicate glass volumetric flask fitted with an air condenser and heated on a hot plate (surface temperature: 250° C) to white fumes, which takes about 2 hours. The resulting clear solution is brought to 100 ml and $[\text{H}^+] = 0.1$ and is ready for extraction.

Counting

All samples are counted for their γ -activity, the following counters being used:

- a thin Si-detector for the fraction containing Hg;
- a well-type Ge(Li)-detector for all other chemically processed samples;
- a flat 40 cm³ Ge(Li)-detector for all unprocessed samples, which are counted together with their polyethylene containers.

Evaluation of Data

The registered γ -spectra are stored on magnetic tape and processed off-line by computer. If a suitable standard has been irradiated and counted together with the samples, the computer is programmed (7) to list the concentrations of all interesting elements in the samples together with their statistical errors.

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DETERMINATION OF THE INDIVIDUAL ELEMENTS

Al, Ca, Mg, Cl

The samples are irradiated for 1 min and measured without any further treatment for 100 s after a waiting time of 1.5 to 10 min. The γ -spectra are checked for the following activities (the half-life and the energy of the evaluated γ -lines are given in brackets):

^{28}Al (2.25 min, 1779 keV), ^{40}Ca (8.7 min, 3084 keV), ^{27}Mg (9.5 min, 1014 keV), ^{38}Cl (37 min, 1642 keV, 2167 keV).

Mn, K, Na, Br

The same samples as used above are irradiated a second time (for 4 min) and measured without any further treatment for 5 min after a waiting time of 20 hours. The following activities are evaluated:

^{56}Mn (2.58 h, 847 keV), ^{42}K (12.4 h, 1525 keV), ^{24}Na (15.0 h, 1369 keV), ^{82}Br (35.3 h, 776 keV).

Hg, Cu, Mo, Cd, As, Sb, Zn, Co

The samples are irradiated to a neutron dose of $2 \cdot 10^{17} \text{ n/cm}^2$ and dissolved as described above after a waiting time of 36 hours. Individual elements or groups of elements are then isolated by the method of subsequent extractions with different metal-dithiocarbamates into CHCl_3 (8); the following fractions are extracted:

by NiDDC_2^* : ^{197}Hg (64 h, 77 keV),
by BiDDC_3 : ^{64}Cu (12.7 h, 511 keV),
by ZnDDC_2 (I) before reduction of the aqueous phase : ^{99}Mo (66 h, 141 keV),
 ^{115}Cd (53.4 h, 336 keV),
by ZnDDC_2 (II) after reduction of the aqueous phase : ^{76}As (26.4 h, 560 keV),
 ^{122}Sb (2.7 d, 564 keV),
by HDDC after bringing the aqueous phase to $\text{pH} 5$: ^{69}mZn (13.9 h, 439 keV),
 ^{60}Co (5.3 y, 1173 keV, 1332 keV).

The organic extracts are evaporated to 3 ml and counted immediately after extraction except for the fraction ZnDDC_2 (I) which is delayed for 24 hours in order to leave sufficient time for the establishment of the $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ and the $^{115}\text{Cd}/^{115\text{m}}\text{In}$ equilibria. Counting times range from 5 min (BiDDC_3) to several hours (NiDDC_2 , HDDC).

RESULTS AND DISCUSSION

It is well known that the dissolution step is critical when either Hg (9) or As (10) is to be determined in an organic sample. Incomplete destruction of the organic material will lead to incomplete recovery of As,

* DDC: diethyldithiocarbamate anion.

Table 1. Summary of analytical results.

Element	Range found in 20 different raw tobaccos		Coefficient of variation	Number of replicates	Capacity/day
Al	200	– 2300	ppm 3%	20	
Ca	1.5	– 4.0	% 4%	20	
Mg	3800	– 6600	ppm 7%	20	30
Cl	3600	– 16400	ppm 3%	20	
Mn	40	– 790	ppm 3%	11	
K	1.7	– 6.2	% 2%	11	
Na	150	– 900	ppm 4%	11	40
Br	50	– 330	ppm 3%	11	
Hg	0.015–	0.060	ppm 5%	3	
Cu	8	– 23	ppm 3%	5	
Mo	0.4	– 1.8	ppm 2%	4	
Cd	1.1	– 2.0	ppm 3%	4	5
As	0.26	– 0.66	ppm 4%	4	
Sb	0.05	– 0.33	ppm 10%	4	
Zn	30	– 79	ppm 3%	4	
Co		~ 0.3	ppm 4%	4	

and too high a temperature will cause losses of Hg and As by distillation. The adopted procedure was checked by spiking inactive tobacco samples with ^{76}As and ^{203}Hg as radioactive tracers; losses through the whole dissolution and extraction steps were found to be less than 1% for As (3 samples) and less than 3% for Hg (6 samples). It is thus concluded that the dissolution procedure works satisfactorily.

A summary of the analytical results is given in Table 1. The range given covers the smallest and largest values found for every element in the analyses of 20 raw tobaccos of different origin. The sensitivity of the determinations was found adequate in the whole range of values encountered in this work. The coefficient of variation* was established by measuring n replicates of one typical sample. Typically, the coefficient of variation is 4%, which is the combined effect of sample inhomogeneity, weighing error, neutron flux gradient, timing errors and errors due to the statistical nature of radioactive decay. Mg and Sb show larger coefficients of variation; while the reason for Sb is not known, in the case of Mg it is due to the very small ^{27}Mg activity compared to the activity of the whole sample.

The capacity is given as the number of samples that one person can handle in a working day; it is seen that while the capacity is quite high for elements that can be determined by purely instrumental analysis, the necessity for dissolution and chemical separations in the other determinations results in a drastic diminution of the capacity.

The time necessary to produce analytical results is short

* The coefficient of variation is the relative standard deviation of one single measurement and defined by

$$100\% \left[\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1} \right]^{1/2} / \bar{x},$$

where \bar{x} is the mean, x_i the measured values and n the number of samples.

if only the handling and cooling times are considered: approximately 1 day for Al, Ca, Mg, Cl and Mn, 2 days for Na, K and Br, and 4 days for the remaining elements. However, the availability of the necessary irradiation, counting and computing facilities can introduce a longer turn-round time.

Finally, a word should be said about the possibilities of determining further elements. Pushing chemical separation further than was done in this work would allow more elements to be determined. To give just one example, adding an extraction step with HDEHP will allow the determination of Sc, La and some of the rare earths; this could be done without significantly increasing the turn-round time and presumably with the same precision. It is also possible to work without chemical separations (2, 3), but in this case a cooling time of one to two months has to be adhered to. This of course increases the turn-round time very much, while restricting the elements that can be determined to those elements giving rise to long-life activities; moreover the precision attained seems to be in many cases considerably less than 10%.

SUMMARY

The determination of 16 elements in raw tobacco by neutron activation analysis is discussed. The 8 elements Al, Ca, Mg, Cl, Mn, K, Na and Br can be determined by purely instrumental means; this leads to a high sample capacity per working day and to a fast availability of analytical results. Contrary to this, the determination of the heavy metals Hg, Cu, Mo, Cd, Zn, Co, As and Sb has to be preceded by chemical separation which is accomplished by extractions with different metal-diethyldithiocarbamates as reagents. The variation coefficient is typically $\pm 4\%$. The lowest and highest values of the concentrations which were found in the analysis of 20 different raw tobaccos are given.

ZUSAMMENFASSUNG

Es wird der Einsatz der Neutronenaktivierungsanalyse zur quantitativen Bestimmung von 16 Elementen in Roh-tabakproben diskutiert. 8 Elemente, nämlich Al, Ca, Mg, Cl, Mn, K, Na und Br lassen sich rein instrumentell erfassen, was einen großen Probedurchsatz pro Arbeitstag und ein rasches Ermitteln der Analysendaten erlaubt. Demgegenüber müssen die Schwermetalle Hg, Cu, Mo,

Cd, Zn, Co, As und Sb nach einer chemischen Abtrennung mit verschiedenen Metaldiäthylthiocarbamaten als Reagenzien bestimmt werden. Der Variationskoeffizient der Bestimmungen beträgt typisch $\pm 4\%$. Die minimalen und maximalen Gehalte, die bei der Untersuchung von 20 verschiedenen Roh-tabaken gefunden wurden, werden zusammengestellt.

RESUME

On décrit une méthode permettant le dosage de 16 éléments dans le tabac brut par activation par les neutrons. Les éléments Al, Ca, Mg, Cl, Mn, K, Na et Br peuvent être dosés d'une façon purement instrumentale, ce qui permet l'obtention rapide des résultats et la possibilité d'analyser de nombreux échantillons dans un temps très court. Par contre, le dosage de Hg, Cu, Mo, Cd, Zn, Co et As exige des séparations chimiques après l'irradiation, ce qui est fait en utilisant différents diéthylthiocarbamates de métal comme extractants sélectifs. Le coefficient de variation typique monte à 4%. On donne les seuils supérieurs et inférieurs des concentrations trouvées dans l'analyse de 20 différentes sortes de tabac brut.

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The authors' address:

*Institut Fédéral de Recherches en Matière de Réacteurs,
CH-5303 Würenlingen, Suisse.*