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NEW HYBRID METHOD

THIN-LAYER CHROMATOGRAPHY WITH X-RAY FLUORESCENCE MICROANALYSIS

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SUMMARY

A new method of identification and determination of nanogram of substances is proposed, which is a combination of separation by thin-layer chromatography and X-ray fluorescence microanalysis of the separated components in the zones on the chromatogram. Scanning of the chromatogram by a collimated beam of primary X-radiation increases the definition of chromatographic zone position and selectivity of the analytical method. This combination of the two methods extends the applicability of each one.

A new method of direct (*in situ*) determination of the substances consists of thin-layer chromatography (TLC) together with X-ray fluorescence microanalysis (X-RFMA)[1]. This hybrid method allows the detection and determination of substances at the nanogram level within small zones of area up to 1 mm^2. It can be applied to the analysis of various natural and industrial materials, *e.g.*, minerals, micro-inclusions, micro radioelectronic devices and semiconductors, small volumes of solutions of precious and toxic substances, etc. as well as in physical–chemical investigations, *e.g.*, of the mechanisms of sorption complex formation, behaviour of the elements in different valency states, composition of ionic forms, etc.

Unlike the popular direct methods of detection and determination of substances from chromatograms, *i.e.*, densitometry[2], luminescence, fluorimetry[3,4], radioactivation[5], the new method does not require treatment of the chromatogram by a reagent, *e.g.*, which gives a colour or a luminescent reaction with the determined ion, or preliminary activation of the element or the introduction of a radioactive "marker". Besides, it is characterized by increased selectivity and low detection limits.

The combination of TLC and X-RFMA has not been described previously

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(see the review on hybrid methods involving TLC[6]). It involves scanning of the sorption layer containing the separated components along the direction of migration of the mobile phase using a collimated beam of primary X-radiation and registering the resulting characteristic X-radiation of one of the elements contained in the analysed substances. This process is carried out after the chromatographic process is over. The scanning is performed with the help of an X-ray fluorescence microanalyzer[7].

Depending on the content of the particular element in a given zone, the scanning can be conducted automatically, with simultaneous recording of the intensity of the analytical line on the recorder or (if the content is small) by means of establishing separate "spots" of the chromatogram under the probe and recording the intensity for a certain time interval (usually 10–100 s). The instrument table on which the object to be analyzed is placed is equipped with a microdrive which ensures location of the sample to within ± 0.01 mm, and the transferrence of the sample under the probe can be controlled visually by means of a microscope. This allows the distribution of elements along the whole surface of the chromatogram to be studied with high accuracy. To correspond with the required resolution, determined by the volume of the chromatographic zones, the X-ray probe is collimated by an aperture of 0.1–1 mm in diameter.

Thin-layer chromatogram on any support (glass, polymeric film, aluminium foil) can be studied by means of this method. When determining the content of elements from their X-ray lines, account is taken of the background due to the sorption layer and the support.

The method was tested by determining microgram amounts of nickel and cobalt after their chromatographic separation. Fig. 1 gives the nickel and cobalt distribution curves after their chromatographic separation from solutions of their chlorides; the mobile phase was acetone–3 *M* hydrochloric acid (99:1), the content of each of the elements in the zone was 1 μg. The chromatogram in Fig. 1 shows the distribution of the analyzed components along the chromatographic plate. The curves were constructed from the cobalt (CoK_α) and nickel (NiK_α) analytical lines upon irradiation of the chromatogram with a tungsten anode. The diameter of the collimated aperture was 1 mm. These curves illustrate the selectivity and sensitivity of the method. The detection limit for cobalt and nickel is $1.0 \cdot 10^{-9}$ g ($P = 0.95$).

The possibility of determining different molybdenum ionic forms previously separated chromatographically during a study of hydrochloric acid solutions was

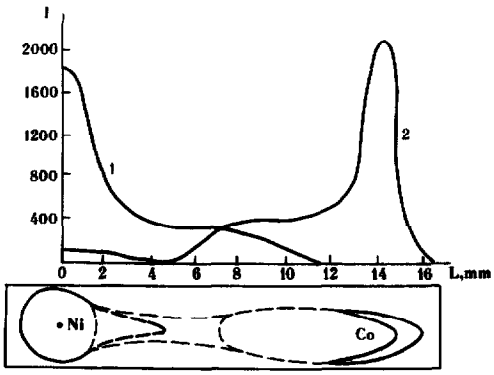

Fig. 1. X-ray fluorescence determination of nickel and cobalt after their separation by TLC.

considered[8]. The overall molybdenum concentration in solution is 0.2–0.5 *M*. Micro volumes of the studied solution were spotted at the start and developed using acetone as the mobile phase. Fig. 2 shows the molybdenum (MoK_α) distribution in the sorption layer according to scans along the direction of migration of the mobile phase with a resolution of 1 mm. The distribution curve reveals the different molybdenum ionic forms, which can be identified as molybdenum isopolymolybdates (the lower zone), cationic molybdenum(V and VI) polymeric forms (the centre of the chromatogram) and molybdenum(VI) chloro complexes (near the solvent front)[8].

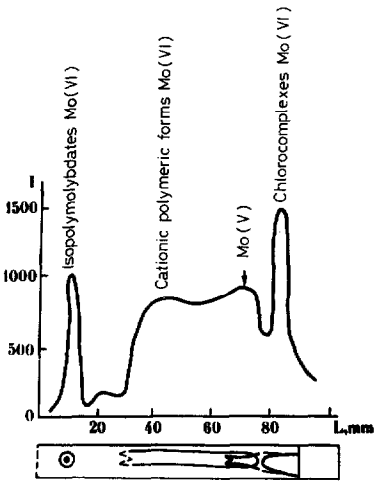

Fig. 2. Scanning of various molybdenum ionic forms in hydrochloric solutions, after their separation by TLC.

The suggested method has great potential and a number of advantages in comparison with established methods. Both inorganic and organic compounds can be analyzed. In principle, virtually all the elements of the Periodic Table, could be determined. The method is characterized by complete selectivity, as every element can be determined on the chromatogram irrespective of the presence of other elements. The absolute detection limit is 10^{-9}–10^{-10} g. The linear resolution of the method is characterized by the diameter of the analyzed zone, equal to 0.1–1.0 mm. The method is not destructive; it guarantees complete security of the chromatogram, including the structure and composition of the determined compounds. Simultaneous recording of several elements in each zone of the chromatogram is possible.

The method can be used to solve analytical tasks which cannot be solved only by chromatography, *e.g.*, the partial separation of two or more compounds, or by the X-ray fluorescence method, *e.g.*, when it is necessary to determine different ionic forms of the same element. Thus the method increases the possibilities of analysis: it widens the class of substances and the number of elements, that can be determined gives the opportunity to evaluate the quantitative correlation of multivalent or other forms of elements and to study the distribution of the components not only along the whole chromatogram but also within each chromatographic zone.

The examples given only partially illustrate the possibilities of the method, although they testify to the expediency of its application to the solution of analytical tasks.

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