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IN THE SCIENTIFIC COUNCIL ON ANALYTICAL CHEMISTRY OF THE RUSSIAN ACADEMY OF SCIENCES

Moscow Workshop on Analytical Chemistry

Nine sessions of the Moscow Workshop on Analytical Chemistry were held over the period since November 1998 to October 1999.

In November 1998, the workshop was devoted to the use of electromagnetic microwave radiation and autoclave sample digestion in chemical studies.

Thus, I.V. Kubrakova and N.M. Kuz'min [Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences (GEOKhI, RAS)] delivered a lecture entitled "Microwave Radiation in Chemical Analysis." Main factors associated with the effect of electromagnetic microwave radiation on analytically important processes such as hydrolysis, complexation, sorption, oxidation, and dissolution were considered in this lecture. An approach to the studies of chemical processes in a microwave field was proposed; this approach included a comparison between the reaction times under conditions of thermal and microwave heating, the yields of formed products, the composition of resulting substances, and the energies of activation. The basic principles of microwave-assisted sample preparation were also formulated.

The lecture "Microwave Radiation in Electrochemistry: The Coulometric Determination of Iridium in Sulfate Solutions" delivered by E.S. Toropchenova, N.M. Ezerskaya, I.V. Kubrakova, T.V. Kudinova, and I.N. Kiseleva (Kurnakov Institute of General and Inorganic Chemistry, RAS and GEOKhI, RAS) was devoted to a combination of microwave sample preparation with electroanalytical techniques. In this lecture, the applicability of microwave fields to the unification of complex iridium species before the coulometric determination of iridium was discussed. Unification of this kind is necessary because chloride complexes are most frequently used as starting compounds in the separation of platinum-group metals and in the determination of iridium, whereas process solutions to be analyzed contain a mixture of mononuclear and polynuclear iridium sulfates of different compositions. The pretreatment of iridium solutions in a microwave field converts a mixture of all the polynuclear oxo sulfate complexes into chloride complexes to stabilize iridium in an oxidation state of +4. This improves the rapidity of the coulometric determination because there is no need for the preliminary electrooxidation of test solutions.

The authors of a lecture entitled "Ruthenium(IV) and Ruthenium(III) Speciation in Hydrochloric Acid Solutions upon Microwave Irradiation," A.V. Bashilov, M.N. Kuz'min, and V.K. Runov [Moscow State University (MGU) and GEOKhI, RAS], reported on the effect of a microwave field on the ruthenium(IV) and ruthenium(III) speciation in hydrochloric acid solutions. The study was performed for revealing the reaction mechanism and accelerating the kinetically inert species of ruthenium(IV) and ruthenium(II) in the luminescence reaction with 1,10-phenanthroline in a microwave field. The authors found that the reaction times of hydration, depolymerization, and reduction of ruthenium(IV) shortened to several minutes in a microwave field, as compared to a duration of several hours (heating in a boiling water bath), months, or years (room temperature). An increase in the power and (or) time of microwave irradiation resulted in an increase in the rates of the test processes (primarily, depolymerization) and in the extent of reaction. A new scheme for ruthenium reactions in a microwave field was proposed.

A.V. Buslaev (MGU) gave a lecture entitled "Basic Principles of the Development of Current Microwave Chemistry" concerning the materials of the International Conference on Microwave Chemistry (Prague, September 1998).

In addition to microwave radiation, autoclave digestion of solids is widely used for chemical sample preparation in studies concerning the composition of substances. V.A. Orlova, Yu.A. Ignat'ev, and N.M. Kuz'min (TsINAO, Russian Academy of Agricultural Sciences and GEOKhI, RAS) delivered a lecture entitled "Autoclave Sample Preparation in Environmental and Biochemical Studies." They discussed the performance characteristics of MKP-04 and MKP-05 analytical modules for autoclave sample preparation and a set of procedures for examining the composition of environmental and geological samples, foods, agricultural products, medicinal preparations, pharmaceutical raw materials, and animal or human tissues. The developed set of analytical procedures efficiently combines autoclave sample preparation with the techniques of atomic spectroscopy [inductively coupled plasma atomic emission spectrometry (ICP–AES), electrothermal atomic absorption spectrometry (ETAAS), and flame atomic absorption spectrometry (AAS)], stripping voltammetry, and spectrophotometry.

The workshop on December 1998 was devoted to the development of atomic absorption and atomic emission spectrometry with the adsorption preconcentration of elements. In the lecture "Flow Sorption–Atomic Absorption Determination of Elements in Environmental Samples" by N.M. Sorokina and G.I. Tsizin (MGU), the optimization of conditions for the flow sorption–atomic absorption determination of cadmium and lead in water, soils, and foods was considered. First, the kinetics of mass transfer of the metals was examined in the course of sorption on polymers with diethylenetriaminetetraacetate groups on the basis of slightly cross-linked polystyrene (PS-DETATA), cellulose fibers (cel-DETATA), and poly(vinyl chloride) fibers (PVC-DETATA). It was found that PS-DETATA can be efficiently used for preconcentrating the metals from solutions with high concentrations of matrix components. The productivity of analysis was 40–60 samples per hour. The procedures were certified by Gosstandart RF (State Standardization Committee of the Russian Federation) and recommended for the purpose of state environmental monitoring.

L.V. Bogacheva and G.I. Tsizin (MGU) devoted their communication entitled "Automated Flow Sorption–Atomic Absorption Determination of Gold, Platinum, and Rhodium in Solutions of Complex Composition" to the flow determination of specified elements in ores and alloys. An efficient nonpolar sorbent (macroporous Amberlit XAD-8) was chosen, and conditions for the preconcentration of noble metals as the derivatives of hydrophobic alkylamines (octyldiethylenetriamine etc.) were developed. The authors found that in the procedure developed, 10^7 to 10^8-fold amounts of ore and alloy macrocomponents have no effect on the results of flow AAS determination of the metals.

With the use of microcolumns packed with DETATA sorbents, standard flow-injection instrumentation, an ICP–AES polychromator, and an IBM computer, conditions were chosen for the simultaneous preconcentration, elution, and determination of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn. This was reflected in a lecture entitled "Study of the Parameters Affecting Analytical Signals in the Flow Sorption ICP–AES Determination of Heavy Metals in Highly Mineralized Solutions" by N.P. Starshinova (GEOKhI, RAS). The software developed made it possible to synchronize the onset of detecting a signal with the onset of the desorption of elements in a plasma. In turn, this provided an opportunity to exert on-line control over the flow-injection unit and to specify the times of analyte sorption and elution. The removal of 99.9% matrix constituents from test samples and the preconcentration of trace elements made it possible to determine heavy metals in water of different mineralization (sea, mineral, drinking, and well water) by ICP–AES.

In January 1999, the results of geological studies performed at the Fedorovskii All-Russia Institute of Mineral Resources (VIMS) were discussed at the workshop. G.V. Ostroumov, deputy director of the institute, considered "Essential Features Required of Analytical Studies in the Geological Examination of Mineral Resources" with the use of various techniques (more than 12) including electron microscopy, x-ray diffraction analysis, IR spectroscopy, luminescence spectroscopy, electron paramagnetic resonance, Mössbauer spectroscopy, etc.

In a lecture entitled "Methodological Principles of the Determination of Ionic Species of the Elements in Naturally Occurring and Technogenic Materials," G.I. Bebeshko (VIMS) presented the results of analysis of minerals and environmental samples by potentiometry. Most attention was focused on the separation of elements as ionic species that produce selective electrode responses. The analytical procedures developed in these studies are highly selective, sensitive, and reliable; at the same time, they require simple instrumentation and are easy to use.

In the lecture "Procedures for the X-ray Fluorescence (XRF) Analysis of Minerals and Products of Their Processing," V.A. Simakov and S.V. Kordyukov (VIMS) surveyed the studies concerning multicomponent XRF analysis performed at this institute. For the complete analysis of rocks and ores, sample preparation procedures were developed with the use of fusion. The measurement error was no worse than 0.3 rel %, and changes in the sample mass as a result of fusion were taken into account. Procedures for the analysis of ores and ore processing products were developed with the simultaneous determination of light and heavy elements with consideration for matrix effects and a background by the method of fundamental parameters. The determination procedures for sulfur and fluorine in combination with other sample constituents were developed. For determining groups of elements with $Z \geq 2\sigma$, methods taking into account matrix effects were developed using incorrectly scattered radiation of the anode line with correlative calibration using virtual reference samples with the use of an internal standard for the direct calculation of matrix corrections. The majority of the procedures developed were metrologically certified and brought to the level of plant or branch standards.

Particular examples of the use of methods available at the institute for solving geological problems were given in the lecture "Analytical Methods for Solving Problems of Applied Mineralogy" by A.A. Rogozhin, L.T. Rakov, and V.T. Dubinchuk (VIMS). In particular, the authors noted that electron paramagnetic resonance makes it possible to elucidate the conditions of formation of mineral deposits, to date geological samples, and to assess the quality of mineral raw materials by determining the distribution of structural defects in minerals. Electron microscopy is used for revealing the finest structural peculiarities of minerals and for determining the speciation and distribution of useful components in ores. Luminescence spectroscopy makes it possible to diagnose minerals in slimes, to contour ore bodies, to assess the size and productivity of ore bodies, and to perform effective separation of ores.

A.E. Bakhur (VIMS) devoted his lecture "Standards and Methods for Monitoring the Radioactivity of Natural Water" to an analysis of new standards and systems for monitoring the radiation-chemical composition of water from host-based systems of drinking water supply. The lecturer considered a list of metrologically certified and approved procedures for radionuclide analysis and their practical applications.

The problems of water analysis were considered at the workshop in February 1999. Yu.M. Dedkov, O.V. Elizarova, and S.Yu. Kel'ina [Moscow Pedagogical University (MPU)] presented a lecture entitled "The Content of the Notion of *Chemical Oxygen Demand (COD):* Methods for Determining COD." All versions of this test method with the use of potassium dichromate, potassium permanganate, and cerium sulfate as oxidizing agents (COD_{Cr}, COD_{Mn}, and COD_{Ce}, respectively) were discussed. The dichromate method should be considered to be the most efficient; however, any deviations from an arbitration procedure result in the incommensurability of the results of determining COD_{Cr}. The authors examined the degree of oxidation of a wide variety of organic substances from different classes under conditions of determining COD_{Cr} and proposed a standard mixture for checking the accuracy of COD_{Cr} measurements.

The following two lectures were devoted to the development of procedures for determining the elements in water at a level of maximum permissible concentrations (MPCs): "Photometric Determination of Zinc in Drinking Water" by O.G. Radugina (MPU) and "Extraction–Photometric Determination of Phosphate Ions at an MPC Level" by S.Yu. Kel'ina (Nikolaev Shipbuilding Academy, Ukraine).

The techniques of local analysis were considered at the session of the workshop in March 1999. Microprobe analysis, secondary-ion mass spectrometry, and electron spectroscopy, in particular, with the use of a scanning spectrometer, were discussed. A lecture by N.N. Kononkova (GEOKhI, RAS) was devoted to the microprobe analysis of samples containing platinum-group elements. The accuracy of the determination of platinum-group elements in geological samples when 15–20 elements were simultaneously determined at each specific site of analysis (when not only superposition of analytical lines of the elements takes place, but also there is some uncertainty about mass absorption coefficients) can be improved by ZAF and PAP corrections. If a reference sample is similar to the test sample in physicochemical properties, the error introduced by ZAF is commensurable to the error of method and amounts to ±5 rel %. However, in more complex cases, the use of a PAP correction in place of ZAF improves the accuracy of determination of some elements by 10–20 rel %.

In the second lecture "Russian Experience in the Quantitative Determination of Impurity Elements by Secondary-Ion Mass Spectrometry" by A.V. Sobolev, S.G. Simakin, M.V. Portnyagin, V.G. Botanova, and I.K. Nikogosyan, the results obtained by a group of scientists from GEOKhI, RAS and Institute of Microelectronics, RAS (Yaroslavl) were presented. The development of a procedure for highly local quantitative analysis of impurity elements in geological samples by secondary-ion mass spectrometry (ion probe microscopy) was reported. Presently, the ion probe at the Institute of Microelectronics, RAS ranks among the world's best ten instruments of this type, which are in the most active operation as applied to earth sciences, and is the only instrument of this type in Russia. The procedure developed allows routine analysis for hydrogen and 20 impurity elements, which are of most interest for solving a wide variety of geochemical problems. The locality of analysis is 10–30 μm. Natural and artificial glasses and minerals (garnet, pyroxene, and amphibole), which differ widely in composition with respect to the concentrations of rare and major elements, certified with the use of precision methods are used as reference samples. The accuracy of determining the elements is 20 rel % or better at concentrations of 1 g/t or higher. The detection limit is 0.002–0.1 g/t. Melt and crystalline inclusions within minerals, phases coexisting in rocks, and relicts of primary crystalline phases in strongly altered rocks.

A.V. Mokhov [Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM), RAS] reported on electron-microscope investigations performed at the institute on spectrometers of two types using wavelength-dispersive spectroscopy (WDS) and energy-dispersive spectroscopy (EDS). The instruments make it possible to perform qualitative and quantitative analysis of samples and to determine the elements starting from boron. The detection limits vary from 0.01 to 0.1 wt % or from 0.1 to 1.0 wt % for WDS or EDS, respectively. The time taken to perform quantitative analysis is 5–20 min or 50–100 s for the former or latter instrument, respectively. The wavelength-dispersive spectrometer requires highly polished test samples, whereas low accuracy in the determination of small concentrations of the elements is a disadvantage of the energy-dispersive spectrometer.

M.I. Lapina (IGEM, RAS) gave a lecture entitled "Analytical Scanning Electron Microscopy: Practical Applications of a Link ISIS Spectrometer." The author considered the capabilities of a new Link ISIS energy-dispersive spectrometer mounted on a JSM-530 scanning electron microscope (Jeol, Japan). As compared with spectrometers of previous generations, the resolution of Link ISIS was improved (from 150 to 133 eV at the $M_nK\alpha$ line); the Super ATW detector window makes it possible to determine light elements (heavier than beryllium). Computer subprograms offer a wide range of opportunities for users, in particular, image generation and processing, rapid qualitative (570 s) and quantitative analysis, and mapping of selected elements in characteristic radiation. The capabilities of Link were demonstrated using an examination of synthetic and natural zircons as an example. The error of quantitative analysis was around 1 rel % for elements with concentrations higher than 5 wt % in the absence of interferences; the error increased in the presence of interferences or at low concentrations.

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