

ELEMENTAL ANALYSIS

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Summary

This article is devoted to one of the most actual problems of analytical chemistry – elemental analysis that is the qualitative detection and quantitative determination of chemical elements in the analyzed samples. It describes the development and improvement of methods of qualitative and quantitative elemental analysis during many

centuries, beginning at the first stage with methods, mainly based on chemical reactions and different processes (precipitation, dissolution, etc.). Nowadays physical methods, based on physical properties of elements and products of their reactions, play the main role in elemental analysis.

Fundamentals and application of various chemical and physical methods of elemental analysis, which differ in nature, assignment, metrological characteristics, are discussed. Among chemical methods of quantitative elemental analysis, gravimetry and titrimetry are described. Spectroscopic, electrochemical, kinetic, enzymatic, chromatographic methods, as well as methods based on radioactivity, of elemental analysis are discussed among physical methods. Spectroscopic methods of qualitative and quantitative elemental inorganic and organic analysis are represented by atomic emission, atomic absorption spectrometry, spectrophotometry, luminescence, X-ray fluorescence, and many others. Special attention is paid to the application of mass spectrometry and neutron activation analysis. Numerous examples of using such electrochemical methods as ionometry, coulometry, and voltammetry are given. It is emphasized, that among all physical methods of elemental analysis, spectroscopic methods are at the first position (about 70 per cent of all analysis are carried out with their help), and nuclear methods are at the second place (about 15 per cent). Mass spectrometry with inductively coupled plasma has the greatest advantages: the absolute detection limit of an element can achieve 10^{-12} g and it is possible to determine 60-70 elements in a sample simultaneously. Application of chemical, physical, biochemical and test methods of elemental analysis in environmental control, criminalistics, cosmochemistry, arts, etc. is discussed.

0. Introduction

Elemental analysis is the qualitative detection and quantitative determination of chemical elements (atoms, ions) in a sample. To detect an element, one should fix an appearance of an analytical signal: the formation of precipitate or characteristic crystals, color change, an isolation of gaseous products, an appearance of a definite lines in spectrum, luminescence, etc. To determine elements quantity, it is necessary to measure a value of an analytical signal: a precipitate mass, intensity of a current, solution absorption, spectrum line, luminescence or radioactivity, a reaction rate and so on. The content of an element is calculated on the base of a functional dependence of the analytical signal value (AS) on a mass or concentration of this element ($AS = f(C)$), which is established by calculations or experiments. To obtain the analytical signal, chemical reactions of different types (acid-base, oxidation-reduction, complex formation), various processes (e.g., precipitation) as well as different chemical, physical, biological properties of elements themselves or products of their reactions, are used.

Methods for the detection and determination of elements are divided to chemical, physical and biological. The most important characteristics of those methods are the detection limit, sensitivity, selectivity, precision, rapidity and price of analysis.

1. Chemical Qualitative Elemental Analysis

Chemical elemental qualitative analysis arose from time immemorial. So, ancient Roman historian Plynii has described an application of a papyrus impregnated with a tannic-galls extract for distinguishing copper from iron: the papyrus became black in a solution of iron sulfate. There are some evidences that at the beginning of the XVIII century Russian Tsar Peter the First has made himself not very complicated chemical analysis for distinguishing sulfur and arsenic, containing ores. R. Boyle (the XVII century) was the first to use hydrogen sulfide as a chemical reagent for lead and tin determination; T. Bergman has shown an important role of hydrogen sulfide in chemical analysis using it for the precipitation of many metals sulfides. At the close of the XVIII and at the beginning of the XIX centuries the majority of reagents for elemental qualitative analysis was known already. In 1829 G. Rose was the first to describe not only reactions for individual elements detection, but the first scheme for the systematic analysis of elements mixtures in his "Handbook on analytical chemistry". Modern hydrogen sulfide scheme for qualitative analysis has been firstly formulated by C.R. Fresenius. Later, in the XX century the other schemes, such as acid-base, ammoniac-phosphate, were also proposed.

In chemical methods of detection, the appearance of an analytical signal in the result of a chemical reaction, is fixed visually, as a rule. Modern elemental qualitative analysis have available numerous selective reactions with low limits of elements detection. To lower limits of detection, one can use different approaches, such as extraction, flotation, drop reactions on filter paper, micro crystalline, catalytic, luminescent reactions, etc.

1.1. Chemical Qualitative Inorganic Analysis

The detection of individual elements in a mixture with other accompanying elements is a rather difficult problem, because all of them can interact with the same reagents with a similar outward effect. Using specific reagents and reactions, makes it possible to detect some elements in mixtures with a fractional method. For instance, starch is a specific reagent for iodine detection (a blue compound is formed), alkali is used for nitrogen detection in ammonia salts. Using different ways to improve selectivity (varying pH values, temperature, masking, changing oxidation degree, etc.) allows us to increase a number of elements, which can be individually detected in mixtures. Application of organic reagents makes easier the fractional detection of elements. A typical example of such reagents is dimethylglyoxime, which can be a specific reagent for the determination of nickel, forming red complex with it under definite conditions (pH, masking interferences).

In those cases when elements can not be detected fractionally, it is necessary to separate them preliminarily. Majority of separation methods are based on selective distributing elements of an analyzed sample between two unmixed phases. The detected elements should be transferred completely to one of such phases. Precipitation, extraction, thin-layer chromatography are often used for elements separation in qualitative analysis. The systematic schemes for analysis of elements mixtures are based on these separation methods. When the precipitation is used for elements separation, the systematic scheme for analysis includes a successive isolation of a small number of elements, their groups,

with the help of group reagents with their following fractional detection, some times additional separation of elements of the same group is necessary. Inorganic (HCl, H₂SO₄, H₂S, Na₂HPO₄, NaOH, NH₃), and organic (8-hydroxyquinoline, dimethylglyoxime, cuppherone) precipitators are used as group reagents. Chromatographic separation of elements (thin-layer and paper chromatography) is based on transferring components of a mobile phase through a stationary phase with a different rate. In paper and thin-layer chromatography, cellulose fiber of a paper and thin layers of different sorbents (metal oxides, silica gels, cellulose) on plates are used as bearers for stationary phases (water, for instance). Various solvents or their mixtures, organic and inorganic acids, can play the role of a mobile phase. Components of a mobile phase form separate zones (spots) on plates or paper strips (chromatograms), which position is characterized by R_F-coefficient, or a relative rate of different components transfer through a stationary phase. Colored zones on a chromatogram can appear immediately, or as a result of developing invisible zones by correspondent reagents, forming colored compounds with elements to be detected.

1.2. Chemical Qualitative Organic Analysis

Contrary to qualitative inorganic analysis, the detection of elements in organic analysis serves as a preliminary identification of characteristic functional groups of organic compounds, containing a definite element. For example, if preliminary studying has shown sulfur absence, it is not necessary to carry out reactions for the detection of SH-, SO₃H- or S-C- groups containing compounds. The main way to detect metals and non-metals (excluding hydrogen and oxygen) while analyzing organic substances, is a distraction of analyte molecules to obtain an inorganic compound which can be identified with chemical reactions. For instance, in order to detect carbon in non-volatile compound, the latter should be heated with KJO₃ at 300-400⁰C for KI formation. The products of this reaction are dissolved then in acidified water, and KI is detected owing to the reaction $5I^- + JO_3^- + 6H^+ = 3H_2O + 3I_2$. Halogen containing organic compounds, after their mixing with copper oxide and following heating, form copper halogenides, carbon dioxide and water. Copper halogenide can be detected by a typical blue-green flame color. While heating nitrogen, arsenic and phosphorus-containing organic compounds with calcium oxide, ammonia, calcium tertiary arsenate and phosphate, respectively, are formed. Ammonia can be detected with the help of an indicator paper. Calcium phosphate is dissolved in nitric acid and then phosphate-ions are precipitated by ammonia molybdate solution, forming yellow crystals of ammonia molybdenum phosphate. Arsenic(V) can be detected using its reaction with potassium iodide, since the product of this reaction – iodine, forms a blue complex with starch.

Metals in organic substances are detected in solutions, obtained after burning to ashes, and following dissolution of analyzed compounds in acids; either treatment with a hot concentrated nitric acid (Carious method) or heating with a concentrated sulfuric acid (Kyeldahl method) can be also used for this purpose. Metals identification can be carried out by common methods for inorganic qualitative analysis.

2. Physical Methods of Qualitative Elemental Analysis

At present, elements are mostly detected with the help of physical methods, which are based on physical phenomena or processes, e.g., an interaction of elements with an energetic current. Among such methods, the method of **atomic emission spectroscopy (AES)**, based on a thermal excitation of atoms of free elements and registration of the optic spectrum of excited atoms emission, should be distinguished first of all. This method was developed by K. Kirchgoff and R. Bunsen (the XIX century). Since 1861 till 1932, 25 elements of the Periodic System (Cs, Rb, Tl, In, Ga, He, Ar, Ne, Kr, Xe, Hf and 14 rare earth elements) were opened with the help of AES method. In 1932, hydrogen isotope – deuterium was opened. The main advantage of the AES method is the possibility to identify with its help a great number of elements in samples, since it allows us to fix a lot of emission lines, which position in the spectrum is individual for each element. The most intensive, so called “last” lines, which are the last to disappear in the spectrum, when the element concentration decreases, are used for elements detection. To improve the reliability of elements identification, it is necessary to detect several lines of the same element in the spectrum.

The main merit of another spectroscopic method – the **method of laser-atomic-fluorescence spectroscopy (LAFS)**, is its high selectivity, which is conditioned by an exceptional simplicity of atomic fluorescent spectrum, and hence, by an absence of a superposition of spectrum lines of different elements.

Methods of X-ray emission spectroscopy (XES) and X-ray fluorescence (XRF) are also used for qualitative elemental analysis. These methods permit multielemental qualitative analysis of solid samples. X-ray fluorescent emission gives an analyst one of the most powerful means for the detection of heavy metals almost in any matrix and complicated substances (e.g., it is possible to detect 1 per cent of tantalum in a sample of niobium with an error ± 0.04 per cent). XRF method can't be used at all for detecting elements lighter than sodium and can be partially applied for the detection of elements, which are situated in the Periodic System before calcium.

Method of **X-ray photoelectron spectrometry (XPS)** allows carrying out indestructible qualitative elemental analysis of solid samples surface, and it is possible to detect any element from lithium to uranium. The analytical essence of qualitative X-ray photoelectron analysis consists of individual values of electron energy in an atom of each element.

Luminescence is also often used for qualitative elemental analysis. Phenomenon of luminescence consists in an emission of atoms, ions, molecules and other more complicated particles, after absorbing energy of the excitation, and this emission is surplus in comparison with a thermal emission of a solid at definite temperature. Not so many metal ions (U, Sm, Eu, Tb, Dy) have their own luminescence in compounds (e.g., minerals). The most interesting practical problem is detection of uranium in rocks and waters, based on the mentioned phenomenon. The luminescent detection of metals is usually based on their reactions with organic reagents, which result in forming luminescent compounds. So, numerous derivatives of oxyazo- and oxyazomethine

compounds are widely used for the detection of Al, Ga, Mg and other elements which form uncolored complexes.

Mass-spectrometric method is widely practiced for elemental analysis of solid organic compounds and materials. This method is based on the ionization of atoms and molecules of a compound, and following separation of formed ions in space and in time. The identification of elements consists in decoding mass-spectrum and a comparison of a location of lines of an element to be sought for, and lines of a known main component or added inner standard. This method allows detection of about 50 elements – admixtures in different solid samples, using special instrumentation.

Radiometric methods, based on measuring radioactivity of natural radionuclides are used for qualitative analysis of geographical samples. Thus, using γ -emission, allows us to find uranium and thorium deposit and to solve other geological problems.

3. Chemical Quantitative Elemental Analysis

There are a lot of various methods, modes and devices for chemical quantitative elemental analysis. Gravimetry and titrimetry were primary methods for quantitative analysis; even now their precision is often higher than that of instrumental methods. Only coulometry and electrogravimetry are characterized with a comparable precision.

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Biographical Sketches

Tatyana N. Shekhovtsova was born in 1947. In 1965 she graduated from the High School and entered the Chemistry Department of Lomonosov Moscow State University (MSU); graduated from it in 1970. In the same 1970 she was employed in Analytical Chemistry Division of Chemistry Department of Moscow State University as a junior scientist. In 1974 she got Ph.D. in Analytical chemistry at the same Chemistry Department of MSU. In 1975 she was promoted to an assistant professor, in 1987 - to an associate professor, in 1996 - to a full professor of Analytical Chemistry Division of Chemistry Department of MSU. In 1996 she obtained the scientific degree Doctor of science in Analytical chemistry. Tatyana N. Shekhovtsova is a Deputy Head of Analytical Chemistry Division of Chemistry Department of MSU; a member of the Scientific Council on Analytical Chemistry of Russian Academy of Sciences, the Head of its two commissions: the commission on analytical chemistry education in universities and the commission on biochemical methods of analysis. As a full professor of analytical Chemistry, she delivers lectures on the basic course of analytical chemistry for undergraduate students of Chemistry Department of MSU, special lecture course on kinetic and enzymatic methods for graduates. Her scientific interests are: development of fundamentals and practice of enzymatic methods in chemical analysis; application of native and immobilized enzymes of different classes and isolated from diverse sources, and apoenzymes for the determination of biologically active inorganic and organic compounds – enzymes effectors (inhibitors and activators). She is an author of more than 200 scientific publications in Russian and International Journals, co-author of three text books for students on fundamentals and applications of different methods of analytical chemistry. She gave oral and plenary presentations at numerous scientific Russian and International Conferences and Symposiums.

Valentina I. Fadeeva was born in 1929. In 1948 she entered the Chemistry Department of Lomonosov Moscow State University (MSU) and graduated from it in 1953. In 1963 she got Ph.D. Now she is an associated professor of Analytical Chemistry Division of Chemistry Department of MSU. She delivers lectures for undergraduate and graduate students of Chemistry Department on various aspects of analytical chemistry. She is a co-author of two text books for students on fundamentals and applications of different methods of analytical chemistry. Her scientific interests are: development of fundamentals of complex formation in heterogeneous systems, sorption and extraction concentration of metal ions complexes; development of hybrid methods for analysis of industrial and environmental samples. She is an author of more than 130 scientific publications in Russian and International Journals, participated in many scientific Russian and International Conferences and Symposiums.