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VIth CZECHOSLOVAK SPECTROSCOPIC CONFERENCE ABSTRACTS

September 1–5, 1980
NITRA

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Organized by

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[redacted]

A

OPTICAL ATOMIC SPECTROSCOPY

DETERMINATION OF THE O/U RATIO IN UO_2 BY INFRARED SPECTRA

Moravec, J., Šára, V., Šourková, L.,

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The infrared spectra /200-1000 cm^{-1}/ of hyperstoichiometric UO_{2+x} /x=0,002-0.1153/ samples were investigated and the dependence of the ratio of absorbances of the transverse and longitudinal optical branches of the infrared-active T_{1u} band at 250-500 cm^{-1} on the O/U ratios was constructed. A rapid method was developed for quantitative determination of the O/U ratio within a range of 2.000 - 2.110. The precision of the method /±0.004 O/U units/ is comparable with those of a no. of destructive and nondestructive methods. The analysis takes 15 min.

B-19

VIBRATIONAL SPECTRA OF MIXED CRYSTALS $NaClO_3$-$NaBrO_3$

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The vibrational spectra of the polycrystalline mixed crystals $Na/ClO_3, BrO_3/$ were investigated for the whole range of concentrations. It was shown by the X-ray analysis that the mixed crystals are substitional ones and do not exhibit any hyperstructure. Both pure materials and mixed crystals crystallize with the symmetry T^4-$P2_13$ /Z=4, the lattice parameters deviate positively from the Vegard law and their magnitudes lie within the interval of 655,9 - - 669,7 pm, $G_S = C_3$/.

The static crystal field yielding the site-symmetry C_3 was studied for the anions ClO_3^- and BrO_3^- in a host crystal which contained 5-15 mole % of investigated material. The possibility of the further reducing of the site-symmetry to the so called effective site-symmetry was also taken into account, i.e. the correlation G_S —— $G_{S\ eff.}$ was introduced into the site and factor-group analyses.

The isotopic effect Cl^{35}/Cl^{37} and Br^{79}/Br^{81} was studied using the Teller-Redlich product rule in approximation of the C_3 site-symmetry and D_{3h} symmetry of the anions.

THE ELECTRON IMPACT, CHEMICAL IONISATION AND FIELD DESORPTION MASS SPECTROMETRY OF SELECTED ANTILEUKEMIC BRUCEOLIDES

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A series of bruceolides have been isolated from a Fijian sample of the Simaroubaceous tree *Brucea javanica.* These quassinoids have significant antitumour activity, marginal in the parent alcohol bruceolide, but of greater activity in the unsaturated esters.

Following separation by column and preparative tlc, the extracts were submitted to electron impact /EI/, chemical ionisation /CI/ and field desorption /FD/ mass spectrometry using the VG Micromass Ltd. ZAB 1F double focusing instrument. Different reagent gases were used in the CI mode to optimise the protonated molecular ion. Molecular ions vary in intensity from less than 1% /EI/ to 100% abundance /FD/ for the same compound.

Two further techniques were used, namely MIKES and linked scans /B/E/. The latter is a popular method for obtaining fragmentation patterns of reactions occuring between the ion source and the first analyser.

C-2

FIELD IONISATION KINETICS: FAST REACTIONS IN THE ZAB REVERSED GEOMETRY MASS SPECTROMETER

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The standard field desorption /FD/ source of the ZAB mass spectrometer has been used in the field ionisation /FI/ mode to determine the kinetics of fast gas-phase reactions. The field ionisation kinetic /FIK/ measurements can be made over the time scale of 10^{-11} to 10^{-9} second.

The ion under investigation is selected using the magnetic analyser and the FI emitter voltage varied. The ion current versus emitter voltage curves for different compounds losing identical fragments by different routes can be compared directly. Calculations on these fast reactions lead to a knowledge of the potential distribution between the emitter and the cathode, the rate constant of the reaction and the parent ion lifetime.

X-RAY PHOTOELECTRON SPECTROSCOPY OF COBALT COMPOUNDS

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Inner-shell photoelectron spectroscopy represents powerful spectroscopic technique for the investigation of bonding in transition metal complexes. In this contribution the X-ray photoelectron spectra of a variety of cobalt compounds have been investigated with particular attention to the satellite lines. The core electron binding energies have been correlated with a calculated charge parameter for the cobalt atoms. Intense satellite lines were observed for the 2p peaks of the high spin Co/II/ compounds. In the case of low spin Co/III/ complexes only weak satellite lines were found which in some cases were a consequence of surface photoreduction. It seems that complexes having larger values of ligand field splitting tend to have smaller satellite intensity. The satellite intensity increases with increasing electronegativity of ligands. The satellites are explained as arising from multielectron excitation which can be interpreted in terms of charge transfer processes using molecular orbital theory. Some other mechanisms leading to satellite appearance are discussed.

Part of this work was performed during the author´s stay at Istituto di Chimica Generale e Inorganica, Universita di Roma.

C-4

USE OF GAMMA SPECTROMETRY FOR THE STUDY OF SURFACE CONTAMINATION OF PURE SEMICONDUCTORS DURING CHEMICAL TREATMENT

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For the preparation of semiconductor detectors as well as for the production of electronical parts made of semiconductor materials the quantitative impurity limitation the semiconductor materials used is a very important factor.

Investigating the influence of impurities in etching agents and rinsing water, respectively, in the course of chemical modification of germanium and silicon surface, gamma-spectrometric analysis has proved to be the best tracing method.

As the model impurities were used isotopes of certain elements, which are characteristic for the possible contamination of the etching and rinsing liquid media.

In the lecture a description of the experiments and a summary of the results are given.

DELAYED FISSION NEUTRON COUNTING BY ^{3}HE-DETECTOR DURING URANIUM DETERMINATION WITH ^{252}CF-SOURCE FOR IRRADIATION

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The possibilities of cylindrical multiwire proportional ^{3}He-detector for determination of uranium by delayed fission neutron technique are discussed. For demonstration purposes, a system composed from approximately 1 mg of ^{252}Cf, polyethylene and paraffin moderators and ^{3}He-detector was assembled.

Detection limits of this system for different types of uranium samples were determined and precision, accuracy, advantages and disadvantages of the method are discussed.

C-6

DETERMINATION OF TRACE ELEMENTS IN STEEL METALLURGY WITH THE AID OF INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

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In the last few years ever increasing attention is paid to determination of trace elements in steel and raw materials, with respect to the required purity of high quality steel products. Some impurities deteriorate mechanical properties of steel to be used in extreme stress conditions, such as the steel for pressure vessels in power stations, while some other admixtures are prohibitive in special steels for nuclear power plants.

A method has been developed in the National Research Institute for Materials for evaluation of the trace elements content in steel, ferro-alloys, slags and slagforming additives on the basis of instrumental neutron activation analysis.

The present contiburion compares the results of INAA using short and prolonged activation in the nuclear reactor at Řež. The achieved detection limits for several elements are compared to those obtained by other conventional analytical methods.

EXPERIENCES FROM OPERATION OF MASS SPECTROMETER MICROMASS 30

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Practical experiences from the operation of mass spectrometer Micromass 30 during more than 1 200 analyses of isotopic ratio $^{235}U/^{238}U$ are given.

Optimum conditions for the sample preparation are discussed. It has been shown, that the special care must be given to the quantity and the chemical form of the material deposited on the filament. Measurement procedure was standardized including heating current magnitude, time of measurement per sample and the way of preparing the filament for sample deposition.

The standard evaluating programme for table calculator HP 9830 was adapted to meet the above given optimum conditions.

The influence of so called "subject factor" is further discussed and the way of operating the machine is given which practically eliminates this influence. Following accuracies have been achieved: for the samples with the isotopic composition near to the value for natural mixture of isotopes the accuracy better than 0,4% can be achieved without use of reference materials. When the non-stabilities of various parameters are eliminated by correlating the samples to a reference standard, accuracies better than 0,1 % are achieved. This value is also usually reported by world top laboratories.

Most the negative influences will be eliminated after the planned modernization of the instrument is finished. By automating the measuring procedure the capacity as well as the accuracy and reproducibility of the analyses will be improved.

PHYSICO-CHEMICAL MASS SPECTROMETRY: ITS SCOPE AND SOME NEW TOPICS

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The early recognized Janus-like character of mass spectrometry has led to a separation of its field of application into analytical mass spectrometry and physico-chemical mass spectrometry. By the latter term the nature of the information supplied by the non-analytical applications is stressed, and also the interconnection of the two fields of MS activity which reflects the more general one linking analytical chemistry and physical chemistry.

As well known, in and by mass spectrometry studies of various chemical reactions and other physico-chemical phenomena can be performed more closely at an atomic /molecular/ level, than by any other method; the processes amenable for this type of investigation being dependent on, and specific to the ion source used. Since the electron impact source has been used overwhelmingly up to now, it is worth while to survey the possibilities offered by other ion sources for physicochemical research. Especially applications of the field ionization sources and the spark ion source are to be dealt with from the point of view of high field chemistry and plasma chemistry.

C-9

THE USE OF THE ELECTRON Si/Li/ SPECTROMETER FOR CONTROL OF MIXTURES OF PURE BETA RADIONUCLIDES

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For some purpose of radiometry it is useful to have the possibility to identify and quantify the components of the mixtures of radionuclides. Si/Li/ spectrometer may be used for this purpose and the analysis may be done out of Fermi-Kurie plot as quality and quantity is concerned. The limiting factor of the method is a distortion of the measured beta spectra by backscattering of electrons.

In this report the method of correction and results of the correction for some radionuclides is described. The correction method is based on the experimentally stated response for monoenergetic electrons. The response function was measured by means of X-e coincidence method for this energy:

E_e - 119,363,624 and 976 keV

It was found that for the energy E_β max higher than about 1 MeV, the correction method does not lead to properly results.

THE SENSITIVITY LIMITS IN GAMMA-RAY SPECTROSCOPY

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The gamma-ray spectroscopy method plays an important role in various fields, such as activation analysis, radioenvironmental studies etc. For these applications the question of minimum observable activities is of great importance. In /1/ and some other studies the limits of a measurement process are given in terms of decision, detection and determination limit /L_C, L_D and L_Q/. The definitions of L_C, L_D and L_Q are associated with standard deviations corresponding to pure background and backround+ peak cases. In previous studies all evaluations of the mentioned limits were performed for simplest case of one peak superposed on linear background. Here the various possible approaches to the measurement limits are discussed and some new, more general formulae are suggested which follow from least-squares analysis of gamma-ray spectra.

/1/ Rogers V.C., Anal. Chem. 42 /1970/, 807

MÖSSBAUER PHASE ANALYSIS OF IRON ALLOYS

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The sensitivity of Mössbauer spectroscopy to the local environment of resonanting nuclei makes possible to use it for the phase analysis. It is especially advantageous for the determination of a small content of a non-magnetic phase in a magnetic matrix. The ^{57}Fe Mössbauer phase analysis in transmission and also scattering arrangements has been used to determine the content of austenite and both magnetic and non-magnetic carbides in steels. For the evaluation of the phase composition from the relative areas of components in Mössbauer spectra a proper correction coefficient reflecting different Debye-Waller factors of phases is introduced. While in the case of austenite this coefficient is known /1/, for the carbides it has been gained by comparison with chemical analyses of steels. As an adjoining result Debye-Waller factor has been calculated for the carbides in transmission arrangement.

/1/ Schwartz L. H.: Int. J. Nondestr. Testing 1 /1970/ 353.

C-13

A DEVICE FOR THE PREPARATION OF BORATE BEADS FOR X-RAY FLUORESCENCE ANALYSIS /OF SILICATES/.

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An attachement was set up to fit the currently produced dental high- frequency furnace, for the purpose of preparing borate glass discs for X-ray fluorescence analysis of rock, mineral, soil and other similar samples.

The attachment consists of a spark source, shallow PtAu3 crucibles, heat- insulating plates and fluxes based on alkaline and alkaline-earth borates.

The produced glass beads are comparable satisfactorily with those obtained with the use of expensive special equipement of foreign origin as illustrated by accompanying slides.

The attachement was produced as a result of cooperation of more institutions.

C-14

GAMMA-RAY SPECTROMETRY IN NUCLEAR POWER PRODUCTION. MONITORING OF THE PRIMARY COOLANT

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Gamma-ray spectrometry in nuclear power production may have number of applications. The basic one is the combined radiochemical and gamma-spectrometric analysis of radioactive materials appearing as a by-product of nuclear power production /effluents, waists liquid or solid, coolants, contaminated materials, nuclear fuel/. In this work an attempt was made to investigate the possibilities of direct gamma-spectrometric monitoring of the primary coolant in a light-water reactor. The main aim of this implementation is the early detection of fuel failure and also the inventory of major radioactive components in the coolant.

Both Ge/Li/-spectrometer mith a multichannel analyser and NaI/Tl/-detector with single-channel analyser have been installed and runned for more than a year. Some results and experience are discussed in more detail. Special attention is paid to possible or observed interferences, possible misinterpretation and to analytical value of the obtained data. It is shown that the high selectivity gamma-spectrometric monitoring may prove to be of interest for nuclear power plant operation.

MODEL EXPERIMENTS FOR THE INTERPRETATION OF THE CARBON ISOTOPE RATIO VARIATIONS OF THE CO_2 OCCURENCIES IN SLOVAKIA

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The interpretation of the isotope geochemical data, supplied at a very high level of accuracy by the present-day mass spectrometers, is often a very delicate problem qiwing to the complexity of the geological processes involved.

As a result of extensive measurements we have found a distribution of the carbon isotope ratios of the Slovakian carbon dioxide occurencies in a range of the $\delta^{13}C$ values between -8 and 0, with a maximum between -8 and -5.

One possible interpretation is to accept mantle origin and a value of $\delta^{13}C$ -8 to -6 for mantle carbon. In this case, however, the more positive data are to be explained. Another possibility is to regard the carbon dioxide as a product of metamorphism of marine carbonate rocks with very considerable change of the carbon isotopic ratio, or followed by mixing with carbon dioxide of organic origin.

Carrying out laboratory model experiments and subsequent mass spectrometric isotopic measurements we tried to find support for the interpretation firstly mentioned, by explaining the more positive $\delta^{13}C$ values as a result of dissolution of limestone by the mineral waters through which the carbon dioxide gas ascends to the surface.

C-16

INVESTIGATION OF THE CHEMICAL COMPOSITION OF IRON METEORITES BY NEUTRON-ACTIVATION ANALYSIS

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Meteorites are the unique species of extraterrestrial matter, available for detailed laboratory investigations.

Essential characteristics of meteorites are chemical and mineralogical composition and structure. They are subdivided on stone, iron-stone and iron meteorites.

At present the great attention is paid to the chemical classification of iron meteorites according to contents and nickel and some microelements ratio in them.

The modern high sensitive method of the neutron-activation analysis in instrumental variant was used for the solution of this problem. Some iron meteorites discovered on the territory of the USSR were studied. As standards the samples of iron meteorites with known chemical compositions were used, namely Sikhote-Alinsky, Henbery and Gibeon.

The samples and standards in form of chips 10-20 mg by weight were irradiated in nuclear reactor under two operation modes- 3 min and 20 hours. Then they were successively measured on the gamma-spectrometer with Ge /Li/-detector and 4000-channel pulseanalyzer in the definite time intervals /5, 50 min and 1, 7, 30 days, accordingly/. So about 30 elements were determined. Their contents in samples was calculated by comparing them with corresponding value in standard.

As a result of the carried out analysis according to contents and nickel, gallium, germanium, irridium, platinum, gold and some other microelements ratio the chemical classification of iron meteorites Yudoma, Aliskerovo, Norinshibir was first carried out and the classification of other meteorites was verified. It is found that the first two meteorites belong to chemical group IV A and III A and the last meteorite is anomalous.

A COMPARISON OF GROUP SEPARATION TECHNIQUES USING NaI/Tl/ AND Ge/Li/ SPECTROMETRY FOR TRACE ELEMENTS DETERMINATION IN BIOLOGICAL MATERIALS BY NEUTRON ACTIVATION ANALYSIS

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Group separation techniques are frequently used for trace elements determination by neutron activation analysis using NaI/Tl/ or Ge/Li/ spectrometry. In this work, both types of procedures were tested for the determination of elements As, Cd, Co, Cr, Cu, Fe, Hg, Mo, /Ni/, Sb, Se, /Sn/ and Zn in various kinds of biological materials. The capabilities of the separation schemes based on distillation and ion-exchange followed either NaI/Tl/ or Ge/Li/ spectrometry were studied in terms of detection limits, accuracy and precision of determination of above mentioned elements in /standard/ reference materials NBS SRM-1577 Bovine Liver, Bowenś Kale, IAEA Pig Kidney H-7 and IAEA Milk Powder A-11. A brief comparison of a price of the analysis using both schemes was also done as determined from necessary experimental and equipment demands. Finally, an attempt was made to minimize a blank value of elements which may appear from processing of irradiated quartz vials.

IDENTIFICATION OF SUPERMAGNETIC PARTICLES USING MÖSSBAUER SPECTROSCOPY

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Mössbauer spectroscopy has become a most important spectroscopic technique for the investigation of ultrafine microcrystals i.e. crystalline particles with the dimension of the order of 10 nm or less. Such particles exhibit a superparamagnetic behaviour. The study of the magnetic properties of such particles is important, not only from a theoretical point of view, but also it may give useful information about technologically important materials such as natural minerals, ceramics and catalysts.

A Mössbauer spectrum is very sensitive to the relaxation time of the magnetization vector of a small particle. It has been shown that the relaxation time varies strongly with temperature and particle volume. Thus temperature dependence of the shape of Mössbauer spectra can be used to estimate the relaxation time and in this way information about the particle volume and the type of microcrystals.

In this contribution we show several results of the measurements on the synthetic and natural samples.

THE USE OF MASS SPECTROMETRY IN ANALYSIS OF ORGANIC DYES AND DYE INTERMEDIATES

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The series of topics solved by analytical chemistry by means of mass spectrometry in the field of organic synthetic dyes research can roughly be divided into three main groups:

1. structure determination of relatively pure or purified dyes
2. analysis of intermediates and starting materials
3. identification of reaction by-products, additives, impurities etc.

Examples are given of using mass spectrometry for analyses of compounds from these groups and a short survey of selected dyes which mass spectrometry has been applied upon in our laboratory is presented.

THE DOUBLY CHARGED IONS OF THE RF SPARK ION SOURCE

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As well known, the doubly charged ions are mostly ignored, when spark source mass spectra are evaluated, the singly charged ions being nearly exclusively used to determine elemental concentrations.

It is to be pointed out however, that in the case of monoisotopic major component elements, and also in cases when the lines of singly charged ions cannot be used for analysis owing to superpositional interferences, the doubly charged ions may present a solution to the analytical problem in question. Beyond that, if the ratio of the singly and doubly charged ions A^{+}/A^{2+} is not sufficiently different from the value 1, any change in this ratio may alter the relative sensitivity factor usually based on the singly charged ions´ relative abundance.

For these reasons we have started a systematic investigation to determine the A^{+}/A^{2+} ratios for various groups of elements as encountered under routine analytical conditions, and also their matrix effect and dependence on sparking parameters. Presenting the results of the first period of this work some conclusions concerning the mechanism

~~of the vacuum spark will be drawn as well, including the possible role of doubly charged ions in the formation of atomic complexes.~~

C-23

DETERMINATION OF TRACE ELEMENTS IN HAIR OF NEWBORN CHILDREN AND THEIR MOTHERS BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

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Hair can be used as an indicator of an environmental pollution. Instrumental neutron activation analysis of hair has been used for the investigation of the influence of polluted environment on the new population. The elements Au, Br, Co, Cr, Cu, Fe, Hg, K, La, Na, Sb, Se, Sm and Zn were determined in hair of newborn children and their mothers. The comparison of elemental composition of hair taken from newborn children and mothers living in two different areas has been made.

VARIABILITY OF VALUES OF GROSS VOLUME BETA ACTIVITY IN NATURAL WATERS CONTAINING ^{226}RA AND U-NAT

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When determining gross volume beta activity, the detectability of different radionuclides greatly varies, some of them are not detected at all. Using Czech surface waters affected by radioactive raw material mining as example, a linear correlation between gross volume beta activity and the values of ^{226}Ra and U-nat volume activity, respectively, on the significance level of $p = 0,05$ was found. The calculated equations of the regression straight lines were in good agreement with the equations of the straight lines derived from the measurement of artificial samples prepared in the laboratory. The extent of the possible contribution of the ^{226}Ra and U-nat, respectively, volume activity to the value of gross volume beta activity in natural waters from the measured results was estimated.

C-25

THE SURFACE MORPHOLOGY OF ION-SELECTIVE MEMBRANE ELEKTRODS

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In the past twenty years the most rapidly developing field in elektrochemical analysis has been connected with the application of ion-selective electrodes. The practical application of these electrodes has parallely been followed by the developing of their theory, though even now are many problems still unanswered.

The response of copper/II/-selective electrodes based on copper /II/ sulphide incorporated in silicone rubber or compressed to pellets is studied with particular reference to electrode behaviour after treatment with various oxidizing agents and regeneration by chemical procedures. Changes in the surface state of the membranes were examined by electron microprobe analysis and photoelectron spectroscopy. The electrochemical behaviour of the membranes can be correlated with surface morphology changes, primarily connected with formation of sulfate monolayers.

C-26

MÖSSBAUER SPECTRA DEPENDENCE ON THE ROLL DIRECTION OF Fe-Si LAMINATION

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Mössbauer spectroscopy has been used for the study of the magnetizing processes of Fe-Si sheets, cut with various angles α with respect to the roll direction. Samples of standardized dimensions /lenght 280, widht 30 mm, thickness 0,35 mm/ have been placed into a yoke, forming a closed magnetic circuit [1]. The intensity of the 2nd and 5th line of the reflected Mössbauer spectrum depends on the angle of orientation. It is possible to determine the change of the effective moments of singular magnetic phases /domains/ inside the material. Two different configurations /1 and 2/ have been chosen for the measurements.

The measurements of the ratio intensities of 2nd to 1st lines /J_2/J_1/ have been made in the geometrical configuration 1. The calculated dependence of J_2/J_1 is shown in this paper for the case of a single magnetic phase with its domains oriented only in the rolling axis.

From the measured curve $J_2/J_1 = f$ /α/ and from the measurement of intensities in the geometry 2 we concluded, that two magnetic phases prevail in the sample for $\alpha = 0$; domains oriented in the axis of rolling and perpendicular to this axis.

The variation of the domain structure for various values of α is confirmed by the measured values of the internal demagnetizing coefficient $N_i = N_i/\alpha/$. We obtained a good correlation between $J_2/J_1 = f\ /\alpha/$ and $N_i/\alpha/$, e. i. both curves give a good information on the homogeneity of the magnetic field inside the sample [2].

From the shown experiments and from the measurements of the reversible permeability as a function of the applied field intensity H for different parameters of α we can divide the magnetizing processes for H acting in an oblique direction to the rolling direction into 3 parts. In the region up to $\alpha \doteq 30^\circ$ the magnetizing process is almost the same as for longitudinal sheet with $\alpha \doteq 0^\circ$, for $\alpha \doteq 60^\circ + 90^\circ$ a perinvar-type process takes place and around $\alpha \doteq 45^\circ$ is a transient region.

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C-27

BIMOLECULAR REACTIONS IN FI IONIZATION OF ALKANE-ALKYNE MIXTURES

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The alkane-alkyne mixtures are especially suitable for studies of bimolecular reactions of hydrocarbons on FI emitters due to the high degree of fragmentation of 1-alkynes. Previous study of behaviour of binary mixtures 1-octyne - n-decane was extended on mixtures containing alkynes of different lengths of carbon chain. The mechanism of fragmentation reactions was studied using deuterium labelled compounds. The results are discussed in analogy with some bimolecular processes involved in chemical ionization of hydrocarbons.

C-28

STATISTICAL CHARACTERISTICS OF SMALL DATA SETS

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Data sets, used for evaluation of analytical data in geochemistry /and in many other fields/, are mostly insufficiently large to permit application of conventional methods of mathematical statistics for determination of the distribution type and for calculation of the statistical characteristics.

These problems could be solved by application of scarcely used methods of treatment of small data sets, based on modification of conventional methods for the number of selected elements.

C-29

USE OF NEUTRON ACTIVATION ANALYSIS FOR THE PROOF OF A NONPROFESSIONAL EXPOSURE OF POPULATION BY ARSENIC

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Several studies were carried out by neutron activation analysis /NAA/ of hair and urine of children to proof an excessive contamination of an environment by arsenic. The samples were colected in surroundings of a coal fired power plant which exhalations containing arsenic are a potent source of the environment contamination.

In this work the study was completed by arsenic determination in blood of studied persons using NAA with radiochemical separation. The arsenic determination is based on extraction of arsenic iodide into toluene from a mixture of sulphuric and perchloric acids which were used for mineralization of samples. The quantitative arsenic evaluation is performed by comparing of gamma-spectra of organic extracts of samples and standards processed in the same way. To the standards some inactive blood was added. When 10 hours irradiation time was applied, the detection limit of arsenic amounted to 10^{-4} µg. The accuracy of the method was tested by analysis of Bowens Kale reference samples.

In samples studied, analysis of hair was found to be most suitable indicator of a nonprofessional exposure by arsenic.

C-30

ABSOLUTE DETECTABILITY OF THE WAVE LENGTH AND ENERGY DISPERSIVE X-RAY MICROANALYSIS

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It is the purpose of this contribution to provide information on extreme limit possibilities of a quantitative analysis of elements with the aid of microanalyzers of the wave length dispersive and energy dispersive types. Great emphasis is put on the determination of the minimum detectable amount of the element and on the application in metallography of the results obtained.

To compare the absolute detectability limits of the two types of microanalyzers the results have been used of the measurements made on identical specimens on thin layers of chromium.

It has been found that with transitive metals of the ferrous group the absolute limit of element detectability is only little dependent on atomic number. With both wave dispersive and energy dispersive microanalyzers its value, determined on chromium, ranges in the order of 10^{-16} g, the value for the energy dispersive microanalyzer JEM-100 C/EDAX being 1.34 times worse than for the wave length dispersive microanalyzer JXA-3A. The results obtained can be employed with advantage in metallography, e.g. in the quantitative microanalysis of submicroscopic structural components extracted by means of extraction replicas.

C-31

COMPUTER METHODS IN MASS SPECTROMETRY

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A review on application of computers in field of mass spectrometry is given. The following topics are discussed: off line systems for treatment of low and high resolution spectra, element mapping, normalization, polyisotopic - monoisotopic transformation, on line coupling. Special emphasis is given to ab initio calculation of theoretical spectra based on fragmentation rules, pattern recognition and selection rules for construction of reduced spectra used for automatic identification of unknown compouds.

A survey of current state of art is given in application of computing systems in controlling the mass spectrometers, including conection with GC or LC. As an example, the combined computer system Dendral, implemented at Stanford Univ., is described.

Finally application of computers in mass spectrometry in Czechoslovakia is discussed.

C-32

STUDY OF ATOMIC ORDERING BY MÖSSBAUER SPECTROSCOPY IN IRON-SILICON ALLOYS

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The atomic ordering is an important phenomenom which influences fundamental physical properties of alloys. It was shown in many papers that Mössbauer spectroscopy can bring new information in this field through its sensitivity to atomic distribution and magnetic perturbations around impurities in ferromagnetic alloys.

The iron rich FeSi alloys are suitable material for study of atomic ordering. It is known that they form the solid solution and ordered phases A_3B and AB. However, there were also theoreticaly predicted further types of order, e.g. A_7B and $A_{15}B$.

We have studied the influence of silicon content, temperature, heat treatment, and plastic deformation on type and degree of order. The best agreement with experimental data gives the theoretical model of inhomogeneous ordering which can be characterised by local fluctuations of Si and by pairs of Si atoms as third nearest neighbours. This ordered structure is stable, the influence of heat treatment and plastic deformations can be neglected.

The dependence of parameters of hyperfine structure on temperature and Si content confirmes the localized interactions and spins in these alloys.

PRINCIPLES AND ANALYTICAL APPLICATIONS OF FIELD IONIZATION AND FIELD DESORPTION MASS SPECTROMETRY

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In a basic and easily understandable introduction the principles of field ionization and field desorption will be outlined. The recent instrumental developments of the techniques as well as the fundamental features for ion formation will be given.

The main emphasis, however, will be put on analytical applications for solving problems in the area of biochemical, medical, environmental research. Recent results in

/1/ ultratrace analysis of toxic metals in biological samples;
/2/ drug and drug metabolite studies using HPLC and field desorption, in particular in cancer-and multiple sclerosis-patients;
/3/ molecular weight and sequence determination of high--mass natural products such as lipids, saponins and peptides;
/4/ isotopic determination of stable- and radio-labelled substances, and
/5/ studies by pyrolysis mass spectrometry of bio-and technical polymers and microorganisms

will be described explicitely.

C-34

MÖSSBAUER SPECTROSCOPY ANALYSIS OF $Fe_{40}Ni_{40}B_{20}$ METALLIC GLASS

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Metallic glass $Fe_{40}Ni_{40}B_{20}$ has been studied by Mössbauer spectroscopy at the temperatures 80 K, 295 K and after the transition to the crystalline state. The samples have been prepared by the roller quenching method. The standard Mössbauer spectroscopy technique was used for the measurement. The Mössbauer spectra consisted of six-line pattern which indicated that the sample is ferromagnetic. For the calculation of the hyperfine field distribution $P_{/H/}$ the binomical and Gaussian functions have been used. From the analysis of the spectra the $P_{/H/}$ function has been determined for both temperatures. The crystaline phases have been identified from analysing the spectra measured after the isothermal heating of the samples.

C-35

DETERMINATION OF TRACE IMPURITIES IN PALLADIUM BY NEUTRON ACTIVATION ANALYSIS

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Trace amounts of Ir, Au, Ag, Pt, Zn, Mn, and Cu were determined in high purity palladium by destructive and instrumental neutron activation analysis /NAA/. The latter version of NAA was employed for the determination of Ir, Au and Ag. Special attention was paid to a new non-destructive method for the determination of silver trace in palladium. The results obtained by both versions of NAA are critically discussed and compared.

C-36

SURFACE ACTIVATION BY CHARGED PARTICLES APPLIED TO THE ON-LINE MEASUREMENT

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Charged particles activation has been developed in the SVÚM for measurement of wear. The thin surface layer containing radionuclides is produced by bombarding a given material with a beam of charged particles. As the material is worn away, the remaining activity can be measured or machine lubricants can be monitored for the presence of radioactive wear debris. A quantitative determination of the wear rate is based on knowledge of the distribution of activity with depth /calibration curve/.

The paper describes the facilities for the on-line wear measurement of a machine lubricant circuit containing radioactive wear debris. Radiation monitoring has been performed using a NaI/Tl/ crystal detector and a multichannel analyzer.

Particular attention has been paid to the choise of conditions for production of radionuclides whose properties best suit the measurement required. Activity-to--depth relationship for radionuclides produced by activation with a beam of high energy protons and deuterons has been estimated in some metals and alloys. Working method for preparing a calibration curve and for quantitative evaluation of the wear rate are referred.

C-37

MASS SPECTRA OF KETIMINE AND ENAMINE TAUTOMERS OF 2-METHYL-3-OXO-3,4-DIHYDROQUINOXALINE DERIVATES

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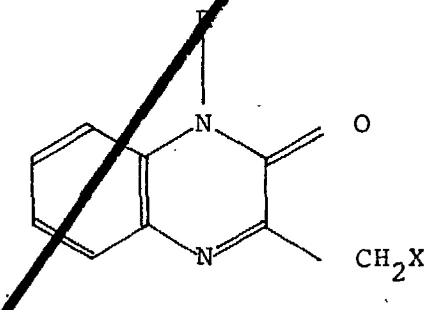
Mass spectra of a series of 17 derivatives with substituents on the methyl group /COOR, CN, NO_2/ activating the ketimine-enamine tautomeric isomerisation and of other 5 similar quinoxalines have been examined. The mass spectral fragmentation pathways are described for each type of the compounds, the fragmentation are confirmed by deuterium labeling experiments. The possibility of characterisation of ketimine /I/ and enamine /II/ tautomers by means of mass spectra is discussed, the results of measurements are compared with literature data for quinoxaline derivatives.



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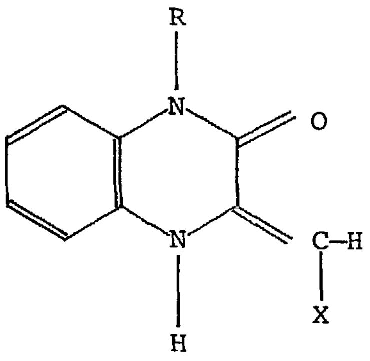

II

X-RAY FLUORESCENCE ANALYSIS OF PHOSPHATE ROCKS

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A method for the determination of phosphorus and calcium in natural phosphates as the raw materials for the manufacture of phosphatic fertilizers was developed. The RFA method was selected for the solution of this problem. The criteria for the choice of this method were: it should be rapid and, at the same time, accurate enough to be used under operational conditions. The currently used methods of chemical analysis do not meet these requirements.

Since raw phosphates, which are processed on industrial scale differ markedly in their characteristics depending e. g. on their provenance, the matrix effects in the studied systems are very significant. To correct these effects, a modified mathematical method Lucas-Tooth-Payne was employed. A series of raw phosphates samples, carefully analyzed chemically for the content of P, Ca, Si, Al, S, Fe, K and Na, was used for the calculation of the interelement influence coefficient α_{ij}. The influencing elements were selected on the basis of the degree of their effect on the element to be determined, considering also the time consumption of the measurement.

The method for the preparation of both the standards and test samplex was grinding of the sample to $< 40\ \mu m$ and its subsequent pelletizing.

All the measurements were carried out using the Philips X-ray spectrograph PW 1410.

THE ANALYSIS OF DEUTERIUM BY MASS SPECTROMETRY

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During many years special instruments and methods were developed for the measurement of the H/D-ratio in water and other hydrogen compounds. The determination of the D-concentration is difficult trough the following facts:

- the quantitative H/D-ratio in natural water is very high /about 10^4/.
- the ratio of the masses is 1/2 and in case of H_2/HD 2/3
- exchange of free hydrogen and hydrogen in water or other compounds
- the formation of H_3^+-ions by ionization in the ion-source.

The sensitivity of the instrument is very high and the resolving power can be small. The potentials and the construction of the ion-source should be so, that the ions stay only for a short time in the source.

In principal, the ratio H/D or D/H or HD/H_2 of a sample is compared with those of a standard. For the elimination of the H_3-ions, two methods are usually used: electronical or calculation. Another problem is the sample preparation. There are some methods; the most practicable is the reduction of water by hydrogen reaction with metallic uranium at 600 - 700 °C /$H_2O + 1/2U \dashrightarrow 1/2\ UO_2 + H_2$/.
The paper is devoted to memory of Dr. Čermak /Institute of Physical Chemistry, ČSAV, Praha/, who died in August 1979.

More than 20 years ago, he was one of the first in the field of mass spectrometric analysis of deuterium.

SPARK-IONSOURCE-MASS SPECTROMETRY IN THE CENTRAL INSTITUTE FOR ISOTOPE AND RADIATION RESEARCH, LEIPZIG; METHODS AND APPLICATIONS

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The paper deals with investigations concerning the preparation of different materials for analysis, some experiences with the mass spectrometer MX 3301 and the semi automatically densitometry and computerized evaluation of mass spectra. Special interest is given to the problem of standards to eliminate matrix-effects and the inhomogeneity of the investigated samples. The reached accuracies are discussed and compared with results obtained by the method of isotope dilution analysis and activation analysis. Finelly, some applications in the field of geology and high purity materials are presented.

C-41

THE NOI-6 N-15 ANALYZER

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Emission spectrometric N-15 analyzers have proved to be a valuable tool in the field of N-15 tracer technique for years. Here, the new type NOI-6 analyzer is presented that meets the growing demands of researchers in this field.

The NOI-6 analyzer consists of the following main parts:

- RF-generator for excitation of a gas discharge
- grating monochromator with oscillating slit for scanning a spectral section
- electronic units with digital display and oscillograph
- integrated system for sample transformation.

The function of the NOI-6 analyzer is explained.
The advatages of the new analyzer are:

- very small quantity of sample /$<$10 µg N/
- short measuring time /10 sec/
- simple to operate
- low costs in comparison to a mass spectrometer.

The NOI-6 analyzer processes sealed gas discharge tubes as well as liquid ammonium samples, the last by means of an integrated discharge tube and a sample transformation system. Quasi continual N-15 measurements in a gas stream are also possible. Integrated function generators give the guarantee to display correct measuring values without further corrections.

C-42

PHYSICO-CHEMICAL CHARACTERISTICS OF PLASMACHEMICAL REACTIONS

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The mass-spectrometry can have various applications within the framework of plasmachemical kinetics. It is an analytical method of defining the products which originate from plasmachemical reactions.

One of the ways of applying plasma-mass-spectrometry is the use of a Quadrupol-Mass-spectrometer for plasmaanalysis.

We describe several examples of reactions of ion-molecules and of the kinetics of plasmareactions.

C-43

ANALYSIS OF NATURAL RADIONUCLIDES BY THE ANTICOINCIDENCE METHOD

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Possibilities of application of multi channel analyzer NTA 1024 for gamma spectrometric analyses for detection of natural radionuclides, by means of scintillation detectors in anticoincidence arrangement, are disciussed.

A special pulse shaper has been developed for this purpose. Its technical parameters and its fundamental function are described.

Fundamental parameters of the detection unit and these of the complete spectrometric chain are presented.