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Československá spektroskopická společnost

8th CZECHOSLOVAK SPECTROSCOPIC CONFERENCE

ABSTRACTS

Section S

SPECIAL SPECTROSCOPIC TECHNIQUES

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Section 8

SPECIAL SPECTROSCOPIC TECHNIQUES

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ABSTRACTS

Volume 3 : Section S (Special Spectroscopic Techniques)

INVITED LECTURES

IS 1

PREPARATION OF SPECTROCHEMICAL AND MICROANALYTICAL STANDARDS

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Abstract

In 1906, five years after its creation, the National Bureau of Standards (NBS) issued the first standard testing and reference materials (SRMs), which were produced to aid the analyst in checking the accuracy of his procedures. Among the first SRMs, ferrous alloys and brasses were prominent. At present, NBS has in stock over thousand SRMs covering a very wide range of application.

SRMs are selected materials having a composition and/or properties relevant to the users. SRMs for chemical and spectrochemical analysis are carefully analyzed by several analysts, and, whenever possible by more than one method. The results are tested by statistical methods for the expression of statistical uncertainties, before their certification.

One basic concern with SRMs is the homogeneity of composition, between and within specimens, of materials for analysis. Large portions of an alloy ingot may have to be discarded in the preparation of the individual samples of SRMs, in order to achieve homogeneity between specimens. Homogeneity within specimens is more difficult to achieve when the analytical techniques to be tested cover small portions of an SRM in every test, as is the case with spark emission spectroscopy, and especially with microprobe analyses. With the electron probe microanalyzer, the sampled volume in steels is about 2 μm in width as well as in depth; techniques such as the secondary ion probes and microscopes sample over even smaller depths. In the analysis of alloys such as high alloy steels, the thermal history of the materia is of the greatest importance, because the volumes sampled in each measurement are smaller than a single grain of alloy. Therefore, SRMs which perform well with macroanalytical techniques are not necessarily satisfactory for microanalysis. Special techniques of testing homogeneity in the micrometer domain are required for this case; it is often observed that in ferrous and other alloys, elements which tend to segregate into secondary phases are more unevenly distributed than the components of primary phases.

Problems related to segregation in the microscopic scale are minimized whenever it is possible to use amorphous or pseudoamorphous materials such as glasses. NBS has issued a series of SRMs of that nature for microanalytical purposes.

In the analysis of particles such as atmospheric dust and asbestos, particulate SRMs are very useful. Their preparation,

however, is very cumbersome, specially when the particle size approaches µm dimensions. In the preparation of glass particles by thermal techniques, the selective evaporation of some components must be avoided. NBS has produced a thin-film standard, and the certification of several particulate standards for microanalysis is presently under way.

IS 2

NUCLEAR SPECTROSCOPY OF LOW-ENERGY ELECTRONS: ITS SCOPE AND SOME NEW TOPICS

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Measurement of the energy spectra of the electrons emitted during nuclear transformations belongs to the oldest kinds of the electron spectroscopy. It has provided enormous amount of information about energy, intensity and other quantum characteristics of the transitions proceeding among neighbouring nuclei or different energy states of the same nucleus.

Today spectrometers (magnetic, semiconductor, proportional, electrostatic ones or their combinations) enable nuclear physicists to scan electron spectra in the range from 10^1 to 10^6 eV. Investigated are continuous energy spectra of electrons and positrons born in nuclear processes as well as discrete spectra of the internal conversion electrons and Auger electrons ejected from the bound atomic states. The radioactive sources and nuclear reaction targets are mostly in a form of the thin solid layers. Since the thickness of these layers is often larger than the inelastic mean free path of the outgoing electrons the spectra are, as a rule, deteriorated by the electron energy losses. Nevertheless, zero-energy-loss peaks, utilized extensively in the X-ray photoelectron spectroscopy (XPS), has been distinguished in the conversion electron spectra, too.

Recent studies of the beta-ray spectrum of ^{3}H in the region of 18 keV, provoked by the claim for a finite mass of the electron antineutrino, stimulated remarkable progress in the development of large-size spectrometers based on improved focusing principles. This surely will have a positive impact on the other fields of the electron spectroscopy. As for the Auger electrons emitted after electron capture decay or internal conversion, their spectra exhibit much lower background than in an usual case of the external excitation of the solid samples.

The most effort has been devoted to the internal conversion electron spectroscopy (ICES)[1/]. Since the emission of the conversion electron results from electromagnetic interaction of the excited nucleus with one of the surrounding atomic electrons, one can expect measurable effects caused by the chemical or physical environment of the atom. In the low-energy region, the following phenomena have been observed: the half-life changes of highly converted nuclear transitions reaching 10 %, up to 30 % changes of the conversion probability for valence shell electrons, appearance of the orbital electron states with unusually high binding energy of about 25 eV, chemical shifts of the conversion lines similar to those in the XPS.

In our laboratory, we employ the electrostatic spectrometer to measure energy spectra of the electrons emitted in the radioactive decay in the region from 40 eV to 20 keV. The resolution we have reached (FWHM = 1.0 eV) is the best one reported in the ICES. In addition to the nuclear physics tasks, we proved that chemical shifts of the conversion lines can provide information about valency state of certain radioactive atoms at no-carrier-added concentration. For example, we determined the Tc(VII) and Tc(V) valency states for the pg amount of technetium produced by decay of the ^{99}Mo(VI) atoms in a solid.

Analysing the shape of the conversion lines we derived the mean lifetime of several N-subshell vacancies in mercury. In our studies of the efficiency of various chromizing procedures applied in electronics, we estimated relative amount of chromium within the 2nm thick surface layer measuring the LMM Auger electrons of 0.5 keV energy in the ^{51}Cr decay. Recently, our spectrometer has been equiped with the Al-anode X-ray tube to perform XPS of the radioactive samples.

Undoubtedly, the reported electron spectroscopy is not only a powerful tool of the experimental nuclear physics but also a promising field of the interdisciplinary research.

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MICROANALYSIS WITH ELECTRON- AND LASER MICROPROBES

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Microanalysis, the investigation of small particles or the determination of the spatial distribution of a certain component in relation to the surrounding matrix, is important for material science, semiconductor technology, surface physics, environmental research, biology, and medicine. To determine elements as well as chemical compounds often spectroscopic methods are used. Microanalysis is possible either using a highly focused electron, ion or laser beam in combination with spectrometers for the emitted signals or by spectroscopic imaging, i.e. the imaging of a specimen area by an imaging spectrometer. This contribution surveys different microprobes and the signals available using electron spectroscopy, X-ray-spectroscopy, mass-spectroscopy, and photoacoustic spectroscopy. Normally we get a high spatial resolution on the cost of the detection limit. As a rule mass spectroscopy has a better detection limit than energy spectroscopy due to a lower background in the spectra. Parallel detection produces improvements in overall efficiencies compared with serial detection.
X-ray-spectroscopy. With electrons or ions of high energy the core shells of the atoms can be excited and we get information on the elements e.g. by characteristic X-ray emission which can be measured either by energy- or by wavelength dispersive methods. On bulk material a lateral resolution of $\delta \approx 1$ µm is possible, on thin foils $\delta \geq 10$ nm. The detection limit is about 0.1 %. With proton induced X-ray emission a detection limit of about 10 ppm has been shown.

Electron spectroscopy is possible either of the transmitted, the reflected, or emitted electrons. The electron energy loss spectroscopy (EELS) for the investigation of thin foils in transmission with primary electrons of about 100 keV has a detection limit of about 100 ppm and a lateral resolution of 10 nm. Electron spectroscopy of the Auger electrons (AES), the secondary-, backscattered, and elastically reflected electrons either with or without ionization and plasmon losses, gives the possibility for surface investigation. Especially AES has become a standard tool for surface analysis. The lateral resolution is about 50 nm.

Ion-spectroscopy allows the determination of either the energy of the ions or of their mass. In ion surface scattering (ISS) the energy of elastically reflected noble gas ions gives information on the mass of the surface atoms. The laser induced mass spectroscopy (LIMS) in combination with a time of flight mass spectrometer allows microanalysis of bulk material or of thin foils. By laser pulses not only ions of elements but also of molecular fragments or even of molecules can be released. The detection limit is about 1 ppm.

Photoacoustic spectroscopy (PAS). The photoacoustic effect is the generation of an acoustic signal by a sample exposed to modulated light. The PA-signal is determined by the optical absorption and the thermal diffusivity of the sample. Therefore, PAS can be utilized to obtain optical absorption spectra. In addition, it is possible to obtain a depth-profile analysis of a substance by varying the modulation frequency of the incident light. PAS not only allows the investigation of solid samples but also of liquids as well as of moisture absorbed or adsorbed on solid material.

Results on the investigations of metal samples, of biological objects and on environmental research are shown, in order to demonstrate the possibilities and limitations of the different microprobes. A qualitative determination of element composition is mostly fairly simple, a quantitative analysis of elemental components or chemical compounds is very difficult and often impossible. A serious problem of all microanalytical techniques is the radiation damage due to the high primary radiation density necessary for a material analysis with a sufficient S/N-ratio.

IS 4

QUANTITATIVE MICROANALYSIS BY X-RAY SPECTROMETRY - MODELS AND PARAMETERS -

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Abstract

The X-ray generation in a target bombarded by electrons is in principle well understood. The impinging electron is decelerated and scattered. Its energy loss can be described by Bethe's law [1] and models also exist for the electron scattering process. To calculate the production of X-rays, the ionization cross-sections, fluorescence yields, relative line intensities and where applicable the Coster Kronig coefficients must also be known.

The X-rays generated within the specimen are attenuated on their way to the surface, and to describe the X-ray absorption the distribution in depth of the X-ray generation in the target material in question, as well as the X-ray absorption coefficients, must also be available. X-rays are also excited by fluorescence, caused by either X-ray lines or by the continuum. The calculation of the continuum fluorescence requires knowledge of the continuum (Bremsstrahlung) generation.

The abovementioned processes can be combined, with the use of random numbers, to construct a large number of trajectories, and the effects are then averaged (Monte Carlo calculations). Alternatively, models for generation, scattering losses, absorption and fluorescence can be constructed and used in the analytical data reduction. In either case, uncertainties in the models and/or associated parameters limit the accuracy of the prediction of emergent X-ray intensities and hence the analytical result. It is therefore necessary to use experimental observations to modify empirically these models and parameters. Besides the direct measurement and the modeling of algorithms for the calculation of X-ray absorption coefficients, the following information can be used for this purpose: tracer experiments to determine the depth distribution of X-ray generation, measurement of electron backscatter coefficients, and the measurement of X-ray intensities obtained under varying conditions from specimens of known composition. Carefully selected standard reference materials are useful in this process.

The use of these data requires an estimate of the quality of measurement and of associated uncertainties. It is also important to apply the laws of error propagation to determine which measurement conditions are conducive to accurate determination of the specimen composition.

In the last few years the accuracy which can be achieved has slowly improved, particularly for measurements of elements of atomic number below 12. More work is needed, particularly for the analysis with oblique electron beams, and for the analysis of thin films and layers, small particles and irregular surfaces.

XRF-ANALYSIS. STATUS AND FUTURE

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Most XRF spectrometers are of types that have been designed for use in a variety of applications. This applies equally to multi-channel, sequential and energy dispersive spectrometers. For example, a given type may be used for the analysis of metals, ceramics or glass, etc. In this sense these types will be referred to below as multi-purpose spectrometers. During their development the emphasis has been on reliability, stability, overall speed, accuracy and ease of operation. All these qualities have reached a high level of perfection and together they are adequate for most routine work in industry and research.

All above types use poly-chromatic excitation with energies of up to 100 kV. Wavelength dispersive measuring channels are often designed for obtaining high intensity at the expense of resolution.
There are certain trends in analytical requirements that would effect the hardware and software of multi-purpose spectrometers or call for spectrometers that are more dedicated to certain analytical tasks.

Multi-purpose spectrometers

There is an increasing demand for a fast (15 min.) qualitative and semi-quantitative analysis of one-off samples in widely different forms and for routine waste disposal samples. The results are to be in terms of concentration intervals at given probabilities for concentration levels of say 100 ppm and upward. The problems are primarily related to obtaining net intensities. A much improved resolution would reduce spectral interferences and make it easier to find reliable background positions. Methods based on high intensity data at lower resolution and number crunching are bound to be less succesful.

For accurate quantitative analysis, the currently used analytical equations can still be improved.

A new model for these equations will be given a first-time introduction. It does not follow the current trend in literature of mostly focussing on the use of higher order correction terms. Instead, the new model enables easy use of a variety of known and partially forgotten analytical methods. For example, the model allows a variable or unknown dilution factor or sample area and gives full account to the use of an added internal standard or a Compton tube line as well as extended concentration ranges. The model is designed such that all interelement coefficients are widely independent of variables like weights. All these coefficients can be calculated from fundamental parameters, that is independent of standards and prior to calibration by regression analysis.

Dedicated spectrometers

There are several known principles that are not used in multi-purpose spectrometers but which would cope with various special analytical problems.

A few of these principles are briefly discussed.

Detection limits are drastically reduced by employing monochromatic or quasi-monochromatic (tube filter) excitation.

Tube voltages of up to say 200 kV would at last enable the measurement of the K-lines of high Z elements. The benifits are a reduction of specimen error (a larger volume is measured) and a reduction of spectral interferences with respect to using L-lines.

Spectrometers with very high resolution are increasingly important in the analysis of chemical states of elements such as in Oxide superconductors.

ADVANCES IN APPLICATIONS OF ENERGY-DISPERSIVE X-RAY FLUORESCENCE METHOD FOR TRACE ELEMENT ANALYSIS

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Energy-dispersive X-ray fluorescence /EDXRF/ spectrometry has proved to be a versatile method in recent years for the simultaneous multielement analysis of samples of different type. The use of more powerful sources of primary radiation as X-ray tubes and synchrotrons from one side and the Si/Li detectors with ultra thin beryllium windows from the other, created a possibility of the determination of number of elements in trace concentrations including even some light elements. The synchrotron X-ray fluorescence /SXRF/ was applied mostly for analysis of biological and environmental specimens. The promising perspective of SXRF is in the analysis of minute samples or in the use of focused microprobe beams for scanning samples with high spacial resolution. Taking the advantage of high intensity of X-ray beam from X-ray tube or synchrotron, the total reflection geometry is succesfully used resulting in diminishing the background and improving detection limits of many elements down to several nanograms per gram. Since the thin sample technique is applied, only one calibration with a single element standard is required for quantitative analysis. Apart from the above mentioned sources of incident radiation, the radioisotopes emitting low-gamma or X-rays are still in use for trace analysis at ppm level, mostly of geological and biological samples. Two approaches are routinely used for concentration determination - Fundamental Parameter method, often combined with so called " transparent" sample technique and a method with the use of standard samples of known concentrations of the elements to be determined. Thin sample technique is used after chemical treatment of a sample and precipitating the metal ions with various reagents, followed by filtration of the precipitate through Nuclepore fliters. Heavy metals in organic matter /plant materials, tissues/ are often determined by the above method after digestion of a sample. As an example the determination of selenium in tissue and several metals in plant material and soil will be discussed in this paper.

IS 7

MÖSSBAUER SPECTROSCOPY IN MATERIAL RESEARCH

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In the last decades, Mössbauer spectroscopy has been increasingly used for the applied research. The range of problems being studied, and achievements in these studies have increased substantially. In our contribution, we want to point out and discuss some applications we are dealing with.

Various problems were solved in our laboratory, including the studies of different kind of ferro-, ferri- and antiferromagnetic materials, synthetic as well as natural. The Mössbauer spectroscopy has been found very useful to indicate the phase composition of the ferrite powders prepared by the wet method after all steps of preparation, as a tool to study; the magnetic oxides used for the recording media as maghaemite and cobalt doped maghaemite; the particles orientation in the magnetic recording tapes; the structural stability and martensite-austenite transformation of steel for nuclear power plants and cryogenic technique; the magnetism of minerals with the aim to specify the nature and the form of iron oxides and its relation to their geophysical history; ferromanganese nodules collected from the ocean bottom, etc. Mössbauer spectroscopy was also used to specify the conditions of preparation of some archaeological and biological samples, to perform the phase analysis of pigments, iron compounds in the polymetallic concentrates, to analyse the intermediate products in the nickel production technological process and corrosion products, to measure the surface and internal tension of metallic parts, to find out the optimal orientation of magnetic domains in the transformer iron sheets in order to reduce the power losses and to investigate some properties of the superconducting materials and amorphous metallic alloys.

In the region of the superconducting materials, the phase analysis of the Nb_3Sn superconductor and its components was carried out and the relation and influence of the technological process on the critical parametres was studied. It seems possible that Mössbauer spectroscopy will prove to be an efficient tool for study of the HTS superconductors.

The amorphous metallic alloys of the type T_xM_{1-x}, where T is a transition metal and M is one, or a combination of more metalloids, are intensively studied by the method of Mössbauer spectroscopy. The reason is that the transition metal is represented by iron and they are of the type Fe_xB_{1-x}. The hyperfine field distribution function P(H) was studied, which provides useful information on the role of different transition metals and/or metalloids on influencing the magnetic interactions, as well as some information on the local structure of metallic glasses. The crystallization processes, and the changes influenced by temperature, and neutron irradiation were studied as well.

The method of Rayleigh scattering of Mössbauer radiation (RSMR) is based on the extreme sensitivity of Mössbauer spectroscopy to very small energy changes. Since recently, this method is being developed as well. It can provide useful information on the crystalline lattice and its vibrational properties. By means of it, integral characteristics of the lattice, as e.g. Debye-Waller factor and Debye temperature can be determined. Thus, the method is very suitable to study the dynamics of solid and viscous solutions, amorphous and crystalline states, phase transitions, etc. The great advantage of this method is that there is no need of presence of the resonant isotope in the sample under study, which increases the applicability of the method to a broad range of samples.

IS 8

THE STUDY OF ELECTRONIC PROPERTIES OF SOLIDS BY MÖSSBAUER SPECTROSCOPY : NEPTUNIUM AND ITS COMPOUNDS

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Mössbauer Spectroscopy is a powerful tool to gain information on the electronic structure of solids via the measurement of the nuclear hyperfine energies. The most common element studied in this fashion is iron. In the present talk the investigation of a more unusual element is presented : the light actinide neptunium. Electronic structure properties in the light actinides are especially complex since the 5f valence electrons can either be fairly localized like the 4f electrons in the lanthanides or fairly itinerant like the 3d electrons in the transition elements. Parameters which affect the degree of 5f localization are the actinide-actinide separation and the hybridization with ligand valence orbitals. Affected are by this in particular the magnetic properties.

First a brief introduction into the Mössbauer hyperfine spectra of the 60 keV resonance in ^{237}Np and their significance in terms of 5f electron structure will be given. Then results on neptunium and its intermetallic compounds will be discussed with emphasis on high pressure Mössbauer data. Of special interest are materials which exhibit the so-called "heavy fermion" properties.

IS 9

SURFACE MAGNETISM OF IRON STUDIED BY IN SITU CEMS

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Results of in situ Monolayer Resolution Conversion Electron Mossbauer Spectroscopy (MR-CEMS) [1] studies of magnetic properties of Fe(110) epitaxied on W(110) single crystal substrate will be presented. The local properties of the magnetic hyperfine field across the film thickness were traced.

The Friedel-type oscillations of hyperfine field were detected near the free (uncoated) Fe(110) surface [2].

The film magnetization versus temperature probed by B_{HF} measurements will be discussed. Experimental results are compared with theoretical results [3].

The ground state hyperfine field at the W(110)/Fe(110) interface was found $B_{HF}(0)=21.4$ T strongly reduced as compared with 34.0 T for the center of the 21-layers film. The B_{HF} vs. T follows the $T^{3/2}$ law.

The spin-wave stiffness constant of the W/Fe and Fe/Ag interfaces is enhanced approximately by a factor 2 in comparison with the center of the film [4].

The spin-wave stiffness constant was found to be a linear function of 1/D where D is the film thickness in atomic layers [5].

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IS 10

FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY

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Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry, first developed by Comisarow and Marshall in 1974[1] has become in recent years a well-established and blossoming branch in the field of mass spectrometry[2]. Especially the development of the tandem quadrupole-, the differentially pumped dual cell-, and the external ion source FT-ICR instruments is very promising for the future of this exciting method.

The basic principle of the FT-ICR method is based upon the motion of ions in circular orbits when they are placed in a magnetic field. Their angular or cyclotron frequency ω_c is then given by $\omega_c = zB/m$, where z is the charge and m the mass of the ions, while B is the strength of the magnetic field. Although the circular motion of the ions is constrained to a plane perpendicular to the magnetic field lines, the ions are still free to move along these lines. To keep the ions in the most commonly used cubic inch cell placed in a high vacuum chamber ($< 10^{-6}$ Pa), a small voltage ($\sim$ 1 V) is applied to the so-called trapping plates which are situated perpendicular to the magnetic field lines. For detection of the ions, a fast swept radiofrequency field of the order of 1 à 2 MHz/ms is applied to one of the pair of plates (transmitter plates) of the cell parallel to the magnetic field lines. This excites the ions translationally and brings them in a larger circular orbit, where they move as an ensemble coherently in phase. The latter motion induces so-called image currents in the other pair of plates (receiver plates) of the cell which are also parallel to the magnetic field lines. These image currents will decrease with time because of collisions of the ions with neutral molecules which destroy the coherent ion motion, so that a transient signal is obtained in the receiver plates. Fourier transformation of this transient signal will give eventually the excited ion cyclotron frequencies ω_c and therefore the masses of the ions.

A very attractive and powerful feature of the FT-ICR method is that in its operation a programmable sequence of pulses can be applied to meet the requirements for solving an analytical problem or studying in detail the chemistry involved in ion/molecule reactions.

In this way it is possible, for example, to switch over from electron impact to low pressure chemical ionization by a simple keyboard control, to isolate ions with a particular m/z value in the cell by application of a series of ion ejection pulses[3] or the so-called notch ejection puse[4-6] where a 180° phase shift is applied at the resonance frequency of the ions to be kept in the cell and to perform MS/MS or multiple MS^n experiments.

By application of a series of ion ejection pulses it has been shown possible recently to isolate selectively in the cell of our Bruker CMS 47 instrument either $C_9H_{10}^{+\cdot}$ or $C_7H_{14}S^{+\cdot}$ ions generated from a 1:1 mixture of the corresponding neutral precursors which requires a so-called front-end resolution of mass selection in excess of 35000 [7]. It will be clear, that this is important not only for analytical studies, but also for detailed studies of the chemistry and mechanisms associated with ion/molecule reactions. This will be shown following a brief introduction to the FT-ICR method and description of ion ejection techniques and an example of a MS^5 experiment by discussion of some selected organic ion/molecule reactions[8].

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HYDROCARBON ANALYSIS BY MEANS OF MASS SPECTROMETRY

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Hydrocarbons can be described by the general formula

$$C_nH_{2n+z}$$

where n is the number of carbon atoms per molecule and z is a hydrogen coefficient which exhibits a typical value for each hydrocarbon type.

Technical hydrocarbon mixtures consist of a variety of individual constituents, the analysis of which is difficult and even impossible if high boiling fractions are to be investigated. For practical purposes it is mostly sufficient to determine the concentrations of the different hydrocarbon types contained in a mixture. Different methods of the hydrocarbon type analysis have been developed for low and high resolution mass spectrometry as well. They permit the determination of up to 25 different hydrocarbon types including such containing heteroatoms in the molecule. Using these methods a relatively rough but complete analysis can be performed.

However, often it is necessary to determine only a single substance or a single class of compounds in a complex mixture. The concentrations of all the other constituents are not of interest then and can be considered as a matrix. For suppressing the matrix the course of the mass spectrometric analysis offers various possibilities. The different experimental steps can be used as gates which allow or disallow passage of the sample. Most of the selective analytical methods use two or three gates. These gates are either fixed or variable.

A separation can be performed already during sample introduction by fractionating the mixture using for example a temperature programmed evaporation. More effective are combinations of mass spectrometry with chromatographic methods. GC/MS combination is widely used for analysing low boiling hydrocarbon mixtures.

Another powerful method for separating the matrix is selective ionization. Owing to differences in the chemical reactivity of the constituents of a mixture selective chemical ionization often makes it possible to ionize only the compounds of interest and to suppress the matrix.

In MS/MS combination instruments are equipped with two analyzers. The first of them is used to separate an ion which is representative of a single component of a mixture and the second to produce a mass spectrum of its fragments. Three scan modes are applied in MS/MS combination. The daughter scanning of selected ions provides information on the types of hydrocarbons contained in a mixture. The parent scanning of an ion characteristic of a particular hydrocarbon type enables us to identify the molecular ions of this type. In neutral loss scanning, screening of hydrocarbon types exhibiting functional groups or heteroatoms in the molecules can be carried out by selecting not individual ions, but ionic reactions representative of these types.

Because of the complex nature of technical hydrocarbon mixtures often two analyzer instruments are insufficient to solve the actual analytical problem. Therefore three analyzer assemblies using an additional analytical gate are applied. They allow the so called second criterion scans to be performed. Up to now these methods have been used only to a lesser extent for analyzing petroleum fractions and coal liquifaction products, but a rapid development is going on in this new field of hydrocarbon analysis.

IS 12

STANDARDIZATION METHODS
IN REACTOR-NEUTRON ACTIVATION ANALYSIS

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Worldwide interest in the role of trace elements in science and technology has led to an increasing need for multielement analysis on a large number of samples. This demand has enhanced the value of purely instrumental, nondestructive reactor-neutron activation analysis /RNAA/ utilizing /n,gamma/ reactions. The number of determinable elements and detection limits may depend on the sample to be analysed but in the present stage of high resolution Ge-spectrometry, up to 40 elements can be determined quantitatively giving detection limits for the remainder. In such circumstances, however, multielement analysis is not feasible using RNAA in its classical form: i.e. co-irradiation and measurement of a standard for each element to be determined.

The recognition of this drawback is not new and from the mid-sixties significant efforts have been made to simplify and modify the standardization procedure. The single comparator method, introduced by Girardi in 1965, was the first pioneering work. Since then a number of novel procedures have been developed as follows:

1969 - De Corte introduces the triple comparator method
1973 - Van Der Linden publishes experimentally determined I_0/σ_0-values for 120 /n,gamma/ reactions

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1974 - Van Der Linden recommends the use of ruthenium as a triple comparator
1975 - Simonits introduces the concept of the k_0-standardization method
1976 - Simonits recommends the use of zirconium as a dual comparator/flux ratio monitor
1977 - Heft publishes the first consistent set of nuclear data for absolute RNAA
1979 - De Corte emphasizes the importance of α-correction and the use of effective resonance energies
1981 - Ahmad suggests a minimalization procedure for flux parameters and nuclear data estimations
1981 - Moens demonstrates a new method for full-energy peak efficiency calculations including gamma attenuation at extended source geometries
1981 - Lin Xiley develops program SINGCOMP for quantitative RNAA using the k_0-method including corrections for true coincidences
1986 - Simonits provides accurate nuclear data for zirconium isotopes
1987 - De Corte provides k_0 and related nuclear data for 112 /n,gamma/ reactions

Recent developments to be presented include corrections for γ- X and delayed γ-γ coincidences, experiences obtained by using the k_0-method for biological sample analysis involving chemical separations, and extension of the k_0-method for very short-lived isotopes.

NAA: A UNIQUE TOOL FOR REFERENCE MATERIAL CERTIFICATION

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Neutron activation analysis (NAA) is only one of many analytical techniques used at the (U.S.) National Bureau of Standards (NBS) for research purposes and for trace element analysis. However, I believe that NAA has unique capabilities when used for high accuracy trace element analysis and particularly for the certification of reference materials.

The NAA technique is well established, and the characteristics of high sensitivity, multielement capability, freedom from most blank problems, plus the ability to analyze many samples non-destructively are often used to justify its use. These characteristics are indeed most useful and important. However, there are a number of additional characteristics which provide profound quality assurance (QA) capabilities which can be built into the analytical system. In considering these "extended" QA capabilities, it is useful to establish the basic analytical system which is common to most spectroscopic methods. This system can be described as follows:

$$\begin{matrix}\text{Incident}\\\text{Radiation}\end{matrix} \longrightarrow \left[\begin{matrix}\text{Excited}\\\text{Species}\end{matrix}\right] \longrightarrow \begin{matrix}\text{Emitted}\\\text{Radiation}\end{matrix} \longrightarrow \text{Detection} \longrightarrow \text{Quantitation}$$

Although the above system accurately describes the activation analysis technique, NAA differs considerably from other analytical techniques because of the nature of the fundamental quantities involved. Further, the entire neutron activation and radioactive decay process is well understood theoretically and mathematically, including errors and interferences. For most real samples, analyses can be simply arranged so the theoretical model is followed exactly, with analytical complexities negligible or completely compensated for between sample and standard.

Illustrations of the fundamental quantities which result in differences between NAA and other spectroscopic techniques include the following:

<u>Incident radiation</u>: The neutrons in a nuclear reactor are isotropic and interact minimally with the sample, thus activating the entire

sample identically (exceptions can be predicted accurately and corrections calculated, with experimental verification).

Excited species: The excited species is nuclear rather than atomic, with lifetimes which are long (minutes to years) and well known. These long lifetimes allow discrimination between elements based on time (halflife) as well as emitted radiation, and permit multiple measurements on the same sample.

Emitted radiation: Almost all NAA utilizes only highly penetrating gamma-rays for detection, allowing the assumption of an infinitely thin sample for most analyses.

Detection: The high purity semiconductor detectors in current use provide spectroscopic data which are highly resolved and virtually lines. Multiple lines with absolutely known emission rates permit verification of the elemental determinations, and the statistical data provided by emission rates can be used along with evaluated errors limits to predict analytical uncertainties.

Quantitation: For highest accuracy, samples are quantitated by comparison to a well characterized standard of the same element(s). High method linearity, use of varying decay times, and total element sensitivity encourage the use of primary standards, i.e., small amounts of the pure element or one of its well characterized compounds. Multiple verification techniques provide measurement redundancy for single samples.

As a result of the above characteristics, there are many quality assurance and quality assessment techniques which can be used to monitor and evaluate the NAA determination, and even to go back and re-evaluate one or more conditions or materials used. Further, when multiple techniques are used to certify a reference material in order to provide an estimate of analytical accuracy, the use of a technique based on nuclear principles along with a technique based on atomic principles helps to minimize the possibility of similar errors between the two techniques.

The above principles will be illustrated with some of the unique NAA QA techniques available and used in the certification of NBS Standard Reference Materials (SRMs). In addition, the preparation and analysis of a new NBS SRM will be described, a botanical material, which will take the place of now unavailable NBS "Orchard Leaves."

ELEMENTAL ANALYSIS OF COAL BASED ON SPECTROSCOPY OF PROMPT GAMMA-RAYS FROM NEUTRON INDUCED REACTIONS

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The analytical method of determination of technologically important elements (Fe, S, Si, H, C) in large volume of coal is described. The method is based on spectrometry of high-energy gamma-rays following interactions of neutrons with atomic nuclei, mainly from neutron radiative capture or inelastic scattering of neutrons.

The experimental arrangement of irradiation facility corresponds with cylindrical geometry. The neutron isotopic source (^{252}Cf or ^{241}Am-Be especially for determination of carbon) with a total emission of 10^7 s^{-1} was centered in the axis and surrounded by the analyzed sample and moderator. The total sample mass in the analyzed volume (40 liters) was about 35 kg. Gamma radiation was detected and analyzed by means of high (Ge(Li)) or medium (BGO) energy resolution detectors. The detector was placed also in the axis of the arrangement. Exposure times were about 1800 s.

On the basis of the well-known paramaters of Ge(Li) detector (typical shape of the experimental spectrum in the arrangement used; efficiencies; resolution) and nuclear data for individual nuclides, the table of expected experimental analytical sensitivities for particular elemental compounds were prepared. This table was designed to select spectral peaks according to analytical importance, to solve some problems connected with spectral interferences and to estimate detection limits for particular elements in different types of coal. The table was also useful for application of the comparator principle.

The Monte Carlo method was used in order to find experimental shapes of spectra for the main analytical lines of the technologically important elements. The modelling mentioned was designed for solving the complex problem of deconvolution of the experimental spectrum measured by scintillator.

The calibration of the analytical system was established on measurments of reference samples. The set of reference samples covered range from sand, different types of brown coal, to black coal. The reference samples were prepared from materials with known elemental composition (by careful sampling and chemical analysis). The method of the standard addition was also used for the check. The main analytical lines were selected as follows: Fe (7645 keV and 7631 keV); S (5420 keV); Si (4934 keV and 3539 keV); C (4438 keV from $(n,n' \gamma)$ process); H (2223 keV). Attention to the matrix effects was also considered. The calibration curves were monotonically increasing and for iron, sulphur and silicon are very close to the lines. The values of the detection limits (weight proportion) were estimated: for determination of sulphur 1 % with Ge(Li), 2 % with BGO; for determination of iron 0.5 % with Ge(Li) and 1 % with BGO detector.

Experimental accuracy achieved with both types of detectors demonstrate the applicability of the method for relatively fast, nondestructive and selective determination of Fe, S, Si, H in large representative samples ($\leq$ 150 kg) of brown coal. The technique with ^{241}Am-Be source and Ge(Li) promises fairly good accuracy also for determination of carbon content. The work is in progress.

The results can serve as a basis for the construction of an analyzer which can be used for efficient control of technological processing and burning of brown coal.

IS 15

SURFACE AND INTERFACE ANALYSIS

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Although the physics of surface and interface phenomena has been studied very intensively the exact description of the nature of surface and interface states is far from being perfect.
New developments and improvements of scientific instrumentation during the last 30 years, however, have provided more detailed information concerning the physics and chemistry of surfaces.
With the complex characterization and empirically derived data the reproducible preparation of thin and ultrathin layers with special surface states became possible.
This development was stimulated by requirements of surface and interface sensitive technologies as in the production of semiconducting circuits. The field of corrosion and catalysis is characterized by growing influence by modern surface results.
On the other hand from the cooperation and interaction between basic research and applied technology new developments and methods escape utilized both in basic sciences and factories.
The ultrahigh vacuum technique e.g. holds for this interactive growing.
After a brief historical view the different probe techniques are discussed principally together with applications.
The most important interaction processes of electrons and X-rays with specimen and their information volumes are presented.

Due to spectroscopical methods energy spectral and chemical information together with imaging allow a complex characterization of the microstructure. The orientation anisotropy can be recorded using angle-dependend measurements utilising polarisation phenomena (e.g. π and σ bonding).
Typical examples demonstrate the performance of the methods, the conditions and the expected developments.

IS 16

TOPICS IN TOTAL CURRENT SPECTROSCOPY

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In the total current spectroscopy(TCS) the electron beam is directed onto the sample surface and the derivative of the current I_T collected by the sample is recorded [1]. The energy of incident electrons is continuously altered in the range of 0 ÷ 30 eV by changing the retarding field between the sample and the last electrode of the gun. The variation of dI_T/dE with electron energy represents all elastic and inelastic interactions of primary electrons with the solid. $S(E) = dI_T/dE$ is equal to $-dI_R/dE$, where I_R is the reflected current. The primary beam current is of the order of several tens of nanoamperes up to about 0.2 microampere depending on the material under the investigation. This enables to avoid unwanted electron stimulated adsorption and/or desorption processes after the preparation of the investigated sample in UHV conditions.

The hitherto existing models of mechanism responsible for TCS fine structure may be represented by two extreme approaches. The first one assumes that the inelastic processes can be ignored, generating only a small component of the sample current in a form of slowly varying function of energy[2]. The TCS spectrum is interpreted as the energy dependence of electron elastic reflectivity coefficient affected by all outgoing LEED-beams. This approach enables to explain the observed features similarly to I-V profiles in LEED experiment.

The second approach assumes an inelastic scattering of electrons in the solid. Such a model proposed by Komolov [3] concludes the dependence of the spectral features on the joint density of empty conduction -and occupied valence bands. The inelastic scattering events of electrons may occur as interband transitions or plasmon excitations. In this approach the reflected current of electrons is in fact an elastic one, and its intensity is modulated by the inelastic component of electrons which underwent inelastic events and remained in the solid, giving rise to the measured current. Although, much of controversy between approaches exists, one may hope to find some convergence if taking into consideration a close relationship of LEED reflectivity with the band structure.

This lecture presents some selected TCS results and shows their resemblance to the results obtained by other electron spectroscopies, like secondary electron emission(SEE), electron energy loss spectroscopy(EELS) and inverse photoemission (IPE) . On the basis of investigatios of various samples of diverse behaviours, i.e. metals(Ag, Sn) and their alloys [4], graphites of different anisotropy[5], and semiconductor compounds (CdTe, $Cd_{1-x}Mn_xTe$) [6], one may find TCS method as complementary to other low energy electron spectroscopies.

Acknowledgments

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ELECTRON SPECTROSCOPIC STUDY OF InP (100)

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X-ray and ultraviolet photoelectron spectroscopies (XPS, UPS) belong among the most important methods for probing the electronic structure of solids. In favourable circumstances detailed information relating surface chemistry (composition, bonding) and band structure can be extracted from photoelectron spectra. Angular resolved photoelectron spectroscopy (ARXPS) enhances the surface sensitivity at grading emission angles giving the possibility of nondestructive depth profiling within the depth of appr. 6.0 nm. In this contribution we report the application of ARXPS and ARUPS to the study of InP (100) face.

InP has become an important material in electronic technology for microwave and high frequency devices. Therefore, understanding, at an atomistic level, of the behaviour and properties of the InP surfaces is not a matter of solely academic interest. As on others III-V semiconductors, the studies has been focused mostly on nonpolar naturally cleaved surface (110) because of difficulties with preparation of non-cleaving surfaces.

InP (100) slides were cut from S doped single crystal having free electron carrier concentration of 5×10^{18} cm^{-3}. A mirror-like surface was obtained by chemical polishing in 0.4% bromine-methanol solution. The final cleaning procedure and measurements were performed using a VG Scientific ADES 400 angle-resolved photoelectron spectrometer. The samples were sputtered by Ar^+ ions (3 keV, 2×10^5 Acm^{-2}, 300 sec., at 150 K target temperature) to remove surface contaminations and oxide layer and then flashed up to 300° C. This treatment produced sharp low energy electron diffraction (LEED) pattern showing the presence of 4x2 reconstructed surface. After keeping the sample for 3 hours at a pressure of 1×10^{-8} Pa, the photoemission from filled surface states, which is very sensitive to any change on the surface, has decreased in intensity even if no traces of contamination were found by XPS. The repeated flash up to 300° C restored the original intensity.

Most identification procedures in previous surface chemistry studies have been done on the basis of chemical shifts of suitable core levels. However, this step alone may be unreliable because of surface Fermi-level pinning, charging and other effects which are to be expected in InP. We analyzed the binding energies of In3d, P2p and O1s lines, corresponding energy separations and line intensities. ARXPS data induced by MgK_α radiation revealed almost stoichiometric $InPO_4$ on the top of the oxide layer and in "depth" and In- rich region with mean concentration of $InP_{0.3}O_2$. Whole thickness of the native oxide is estimated to be 1.5-2.0 nm.

Sputtering of InP by Ar^+ ions, as an important technological step, caused substantial changes in composition and morphology. Resulting In/P concentration ratio as high as 3 is not an exception. Severe changes in surface morphology which may result in In globules formation may be suppressed by applying lower target temperature during sputtering.

The flash at 300° C has recovered the damaged surface structure resulting in InP (100) 4x2 reconstruction. This surface is P-rich within two topmost atomic layers with extended P depleted region of about 3.0 nm below the surface. The particular shape of concentration - depth curves seems to be dependent on cooling rate just after the flash.

Recent angle-integrated UPS experiment on InP (100) surface [1] revealed a large photoemission intensity near the valence band edge ascribed to filled surface states in this energy gap. We have repeated their experiment, tested the character of the photoelectron intensity to be sure that it is photoemission from filled surface states and we continued to map the gap surface states in $\bar{\Gamma}\bar{X}$ and $\bar{\Gamma}\bar{M}$ directions of surface Brillouin zone. In conclusion, from the results of ARUPS, LEED and ARXPS it follows that the nature of the gap surface states is connected with phosphorus atoms on (100) surface.

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POSTERS PS 1 - PS 25
PS 100
PS 27 - PS 31

X-ray Microanalysis

PS 1

NORMALIZATION OF COMPOSITION AND CONVERGENCE OF ITERATIVE ZAF CALCULATIONS

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Convergence of correction procedures in quantitative X-ray analysis is related to a type of iteration technique. As it was shown by Springer [1] all techniques differs only in the way of evaluation of a value of $\delta f_i/\delta c_i$, thus they differs in the speed of approaching the composition fulfilling the relation:

$$C_i = k_i * f_i(C_1, C_2, \ldots, C_n) \quad i=1,2,\ldots,n \tag{1}$$

Normalization during the iteration cycle helps to obtain better estimation of true elemental weight concentrations [2] but it is not crucial and has not found much interest in literature. Probably only one normalization formula is used:

$$C_i(\text{normalized}) = C_i/\Sigma C_i \tag{2}$$

which has neither physical nor mathematical motivation.

In the statistical approach on few assumptions another normalization formula [3] can be obtained:

$$C_i(\text{normalized}) = C_i + (1-\Sigma C_i) * \sigma^2_{ci}/\Sigma\sigma^2_{ci} \tag{3}$$

where σ^2_{ci} is the variance of calculated concentration connected with the variance of the relative intensity by the relation $\sigma^2_{ci} = \sigma^2_{ci} * f^2_i$

Conclusions

1. In the case of high absorption the use of proposed normalization formula leeds to increase the convergence of simple iteration technique.
2. It also increases the precission of chemical composition evaluation for the element estimated with the lowest reliability.
3. In the case when a total of element contents differs from unity less then $2*(\Sigma\sigma^2_{ci})^{0.5}$, this difference can be explained statistically, and the final concentrations should be normalized.

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PS 2

TRUE DIFFUSION PROFILES BY PROCESSING OF X-RAY MICROANALYSIS EXPERIMENTAL DATA

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Determination of true diffusion profiles (i.e. elements concentration profiles) becomes difficult when the size of diffusion junction is comparable to the diameter of an X-ray signal source.The main role plays here horizontal diameter of the latter; the source depth is the separate question.In such a case an experimental concentration profile is the convolution of true profile and the source emission distibution function.There are several data processing routines leading to the true profile (for instance the fast Fourier transform).In this paper another method has been applied, namely the least squares fitting of parametrized convolution to experimental data.The arbitrary choosen function containing the junction width parameter is used to describe the true profile. The source emission distribution function has been derived to be the Gaussian distribution. The least squares fitting leads to the correct form of true concentration profile by minimization of the following expression

$$S^2(\alpha,\beta) = \sum_{j=1}^{N} \frac{1}{N}\left[y_j - F(\alpha,\beta;x_j\right]^2$$

where y_j -experimental data and $F(\alpha,\beta;x)$ is the parametrized convolution function.

TESTING HOMOGENEITY OF SOLIDS BY AUTOCORRELATION - FUNCTION

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Testing homogeneity along a line-scan usually is done by analysis of variance. The necessary determination of the experimental error often is connected with a loss in lateral resolution and/or with a loss of sharpness for the statistical test.

A line-scan can be seen as a sequence of data similiar to a time-series. Then the autocorrelation-function / acf./ gives information about the homogeneity of the investigated material with reference to the method used for chemical analysis. acf furthermore enables the detection of very low gradients in the composition of the material as well as the detection of periodicities. These theoretical predictions could be confirmed by measurements by microprobe.

DISCUSSION OF ERRORS IN AN INTERLABORATORY X-RAY MICROANALYSIS TEST

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Interlaboratory test of X-ray microanalysis involving the determination of elemental composition of a standard austenitic stainless steel containing: 18.16%Cr, 11.06%Ni, 1.43%Mn, 0.56%Si, 0.143%Cu i 0,029%Co, was described [1].
Particular attention was paid to the accuracy of individual results. It was found that 48 of 87 determinations carried systematic errors. The most frequent errors were in determination of Co, Cu, Mn and Si /relative error greater than 10%/. By means of MAGIC IV correction program the relative intensities k , for the actual elemental composition of the sample, were calculated. Then,experimental and correction errors were assessed. It was established that the experimental errors had influenced very strongly the accuracy the results, especially in case of the low concentrations of the elements. The overlapping of $K_{\alpha 1,2}$ lines of Cu, Mn and Co with $K_{\beta 1,3}$ lines of Ni, Cr and Fe respectively resulted in high values for the former elements. Moreover, the close neighbourhood of these lines made background correction difficult. The presence of satelite line close to Si $K_{\alpha 1,2}$ line probably caused the overestimation of Si content by some laboratories.
Test results were also used to assess the methods of microanalysis. After excluding widely deviant determinations /about 18 % of results/ good agreement between mean determinations and actual values was obtained /absolute error less than 0.3 %/ and satisfactory accuracy of determinations for elements in concentrations of more than 10 %.

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EDMAX - A NEW DEVELOPMENT OF THE ENERGY DISPERSIVE MICROANALYZER OF X-RAYS

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It is reported about the system of energy dispersive spectrometry of X-rays developed for use in the electron microscopes. The most pronounced feature of the conception is the attention paid to analytical imaging facilities in X-ray mapping mode.

The cooperation with academic institutes in GDR and Hungary was utilized to assembly the high performance equipment. The cryostat and digital electronics were made in Brno, while the detector and signal electronics were obtained from ATOMKI Debrecen and A/D Converter from ZWG Berlin. The off-line software for the spectrum processing is implemented according to algorithms elaborated in ZWG Berlin and TU Dresden.

The technical parameters of the system will be documented together with results of the first testing experiments.

MIGRATION OF ALKALINE IONS IN MICAS

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During the EPMA of micas the alcaline ions migrate from the irradiated volume. Aim of this work is to determine the factors effecting migration of alkaline ions and to find optimal conditions of the analysis.

The following factors were investigated:

a) Irradiation parameters; accelerating voltage, absorbed electron current and the diameter of the beam spot.

b) Different orientation of mica crystals to the primary beam of electrons.

c) The influence of chemical composition of different types of micas on the rate of migration.

d) The influence of different structural parameters of investigated micas on the rate of migration.

The mechanism of migration was studied, and simple model of this process is presented.

ELECTRON MICROPROBE DETERMINATION OF THE GRAIN BOUNDARY DIFFUSION COEFFICIENT OF CHROMIUM IN STAINLESS STEELS

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EXPMA method was used for determination of the grain boundary diffusion coefficient $D\cdot\delta$ of chromium in stainless steels during heat treatment at 1050°C in air, when a scale rich in Cr builds up on the surface. Diffusion of Cr to the scale is faster along grain boundaries. This makes them poor of this element [1].

Calculation of Cr diffusion coefficients were based on the Fisher model [2]. The metal-scale interface migration was taken into account [3]. The misorientation angle of the adjacent grains was about 45°. Using EPXMA chromium concentrations were measured perpendicular to the grain boundary in various distances from the surface. The distances between points in which the Cr counts were measured were about 1 μm.
The grain boundary diffusion coefficients on the basis of 90 to 100 measuring points were determined. Standard deviation was calculated at $\alpha=0.95$.

$D\cdot\delta=1.38\cdot10^{-13} \mp 0.17\cdot10^{-13}\ [cm^3\ s^{-1}]$ for 00H18N10
$D\cdot\delta=3.60\cdot10^{-12} \mp 1.14\cdot10^{-12}\ [cm^3\ s^{-1}]$ for 1H18N9T

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NON-METALLIC INCLUSIONS IN AUSTENITIC Cr-Ni STEEL

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Modern types of corrosion resistant austenitic Cr-Ni types of steel have been developed for the most advanced applications in chemical and food industry and have also been successfully used for the production of surgery implanates.

It is obvious that for such advanced applications the steel must have an optimal chemical composition,structure and other properties,above all the corrosion resistivity. One of the most important structural factors having influence on the resistivity of austenitic steel against corrosion is its purity,i.e. the kind, amount,size and phase composition of inclusions.

The aim of this paper is to obtain a detailed characteristics of the purity from these points of view. Five samples of high quality austenitic Cr-Ni steel were studied.

For all samples the average maximal impurity according to the GOST was determined by optical microscopy. Morfology of the inclusions was studied and the identification of inclusion types and their chemical composition were determined using an energy dispersive analyzer KEVEX.

It has been proved that energy dispersive analysis can be successfully used to determine both the chemical composition even of the very small amount of inclusions present in the sample in a very dispersive form. Using the method of elemental X-ray images various parts of the heterogenous inclusions have been identified.

Principal results of inclusions analyses,viz. identification of components of their heterogenous complexes are presented.

EPXMA INVESTIGATIONS ON THE COMPOSITION OF BORIDE LAYERS ON STEEL

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Boride layers on steel are used in many cases to increase the wearability of materials and products. The analysis of these layers by EPXMA is not simple because the very long-wave B-K_α radiation to detect is very difficult. These difficulties are not only the inaccurate knowledge of mass absorption coefficients and the difficulties at the determination of the background of bremsstrahlung radiation but also the influence of the chemical bonding to the shape of the X-ray spectral lines.

We have measured the mass absorption coefficients of the B-K_α radiation in Fe by a method based on BEER's law /1/ and the self-absorption coefficient by use of the "thin film model" of DUNCUMB and MELFORD /2/. Furthermore we have determined an analytical expression of the intensity of bremsstrahlung of the B-K_α radiation as a function of energy and atomic number. The measurements are similar to those which are described for short-wave X-ray radiation by BÖCKER /3/. The so-called "transformation to the space of representation", described by /4/, was used to characterize the influence of different elements of alloys on the shape of B-K_α emission lines. The results of these investigations are demonstrated on different examples.

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EDS AND XRD STUDY OF $SmBa_2(Zn_xCu_{1-x})_3O_{9-\delta}$

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It is known that perovskite type structure ($ReBa_2Cu_3O_{9-\delta}$) exhibit superconductivity at temperatures below ≈ 90 K. The substitution of other ions for Cu is interesting because of the great importance of Cu-O interactions.

The samples $SmBa_2(Zn_xCu_{1-x})_3O_{9-\delta}$ (with x = 0, 0.1, 0.2, and 0.3) were prepared by solid state reactions. The phase composition was determined by X-ray diffraction, metallography and EDS analysis. The x-ray diffraction analysis showed that the $SmBa_2(Zn_xCu_{1-x})_3O_{9-\delta}$ for all Zn concentrations exists as a single phase material with the perovskite structure. For x = 0 the perovskite phase has an orthorombic lattice while in the case of Zn dopped samples the perovskite phase has a tetragonal lattice. EDS analysis showed that in all cases exists the phase of composition formula $SmBa_2(Zn_xCu_{1-x})_3$. For x = 0.2 and 0.3 were determined in the structure small regions that were probably ZnO, as the EDS analysis of them revealed the only presence of Zn.

From the results we can suppose that substitution of Zn for Cu in the perovskite-type phase affects the orthorombic-tetragonal transformation and the substitution is possible till x = 0.3.

PS 11

EDS STUDY OF THE PHASE STRUCTURE IN Sm-Ba-Cu-O

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The new superconducting properties of materials based on Cu oxides which have been recently observed has caused an apparent investigation of their multicomponent systems. EDS spectroscopy is useful method which properly complet the other methods of structure study of such materials.

The composition of the phases presented were found out by investigation of the structure of sintered oxides of Sm, Ba and Cu. Their volume ratio changed accordingly the mutual ratio of the elements. EDS analysis enabled to optimize the sintering of pulvers till the homogeneity of the structure was achieved. It was confirmed that the reaction in the solid state realized intensively. The comparision of the phase structure determined by XRD analysis and the element composition of the phases with the results of temperature behaviour of electrical resistance enabled to suppose that the superconducting properties are in connection with the presence of orthorombic $SmBa_2Cu_3O$ perovskit type phase. This assumption was confirmed by preparing the monophase sample of such composition. The sample showed the transition temperature to the superconductivity state at 86 K.

DISTRIBUTION OF SOLUTES IN THE γ - DENDRITS IN THE EUTECTIC $\gamma/\gamma'-\alpha$ COMPOSITE.

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The $\gamma/\gamma'-\alpha$ composite material with 1 wt.% Fe prepared of technically pure metals at $R = 2.78 \times 10^{-6}$ mxsec^{-1} contains 14 vol.% of nickel-based primary dendrites. Their mean linear size is 210 μm. Temperature of boundary of α - dendrites is the function of stabilizing parameter $G \times R^{-1}$. At the selected conditions of oriented growth of difference of temperatures between the dendrite boundary and eutectic mixture of phases makes 11K. The growth changes of composite are accompanied with the change in distribution of solutes in the solidified γ -dendrites. Molybdenum exerts the highest susceptibility to microsegregation in solid state. The change $(c_s)_{Mo}$ is the function of volume fraction of solidified ingot g. Distribution of of solutes is actually uniform along the whole length of dendritic arm.

THE USE OF ENERGY DISPERSIVE X-RAY MICROANALYSIS IN THE STUDY OF PROTECTIVE COATINGS ON METALS

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In order to charakterize protective coatings on metals,it is often necessary to determine their local composition. There exist a number of spectroscopic methods applicable for determining the distribution of individual elements in the coatings. In the present contribution,examples of the use of energy dispersive X-ray microanalysis are described.Two sets of samples were analyzed:

- steel samples with coatings prepared by laser surface alloying
- steel samples covered by enamel coatings

Laser surface alloying enables the formation of rather homogeneous coatings composed of iron-base alloys on unalloyed steel. During the coating deposition, the surface is scanned by a laser beam. The alloing material is added before or during the irradiation.The concentration mapping by an energy dispersive X-ray microanalyser showed clearly the differences in the distribution of the alloing elements in case of continuous surface alloyed layer and, on the other hand, in case where the coating was composed of separated non-overlapping tracks.

The adherence of enamel coatings to the steel substrate depends critically on the presence of "adhesion oxides"/mostly CoO or NiO/. During the heat treatment of the system, the reduction of Co^{2+} or Ni^{2+} occurs in the enamel melt at the steel surface, which results in the formation of Fe-Co or Fe-Ni alloy particles in the enamel coating near the steel-coating interface.

The X-ray microanalysis and in particular the concentration mapping were able to show that the composition of these metallic inclusions in the enamel coating is very different from that of the substrate. Thus, it was possible to confirm the validity of the electrochemical hypothesis of the adherence of enamel coatings to steel.

INVESTIGATION OF DIFFUSION OF SPRAYED NiCrBSi ALLOY COATINGS.

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Within the range of known methods of heat spraying the technique of remeltable coatings has been attracting most attention in the recent years.It has been due to very high functional qualities of the coatings,e.g.very good abrasive resistance,high resistance to corrosive factors,and very good adherence to the base.

The remeltable coatings are produced from PMNi 50 powder /its contents being C+Si+B-6-9per cent,Fe-3-5per cent,Cr-5-8 per cent,and Ni-the remainder part/in two stages:1/spraying of the coating material,2/remelting of the coating that has been sprayed in the first stage.

In the present study both theoretical and experimental work concerning the method of NiCrBSi type metal remeltable coatings for regeneration of worn machine parts have been prepared.The samples underwent milling and grinding prior to spraying.The coatings have been sprayed on by means of KNP-1 metal spray gun at oxygen pressure of 0.25MPa and acethylene pressure of 0.03MPa.

The microstructure has been observed as well as the diffusion of the sprayed coating chemical elements has been tested by means of CAMECA MS 46 electron microprobe.

It has been found that the coating to base binding mechanizm is of diffusional character.The conditions conductive to the diffusion of the constituens are created during remelting of the coating.It has been observed that the metal remeltable coatings are of remarkable functinal quality.

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CONCENTRATION PROFILES IN THE UNDERLYING ALLOY DURING THE OXIDATION OF Fe-Cr-Mn ALLOYS

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Compositional changes in Fe-Cr-Mn alloys during the formation of Mn_3O_4-rich scales have been measured by electron probe microanalysis and calculated by solution of the appriopriate transport equations.

Numerous investigations have schown that the manganese can play an important role in the oxidation behaviour of this austenitic heat resisting steels.

The manganese concentration as a function of depth by step-scanning at 2,4 μm interwals. The microprobe spectrometr was tuned to the manganese K_α radiation and counts were carried out for 10 s. The metod did not reguire accurate knowledge of the level of background radiation since the analysis is based on the change of manganese concentration as a function of depth.

INVESTIGATION OF THE EFFECT OF HEAT TREATMENT ON THE MICROSTRUCTURE OF Co-BASE SUPERALLOY BY SEM, TEM AND X-RAY MICROANALYSIS

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Co-base superalloys are used as the heat-resisting, wear-resistant and corrosion-resistant materials in aircraft industry, energetics and medicine. This paper presents the results of the investigation of the cobalt alloy used for surgical implants in orthopaedic. This alloy consists of 19wt% Cr, 10wt% Ni,0.74 wt% Mo, 0.7wt% Ti and 0.01wt% C, balance Co. The alloy was vacuum casted and forged. All specimens were heat-treated by solutioning under an argon atmosphere for 1,2 and 4 h at 1373-1573 K and water quenched. Then the some specimens were aged for 5h at 923 K and air-cooled.

The microstructure, phase composition, hardness and electrochemical corrosion resistance after heat treatment were determined. Chemical segregation was examined by MAR. Phase analysis was caried out using X-ray diffractometry. The microstructural examinations were performed using optical, scanning electron and transmission electron microscopy. The change of grain size, lattice parameter, the size of precipitates and the deformation strueture were examined too. The methods SEM and TEM were particulary useful to observe the secondary prepicitates, slip planes and stacking faults.

As a result of the investigations it was found that this examined alloy is a two-phase material. In the wrought and solution-treated material the dominant phase was fcc but there was the hcp phase too. Aging heat treatment promoted transformation of the fcc to hcp phase. There was the titanium carbide as primary precipitates in this alloy. In the definite hot-working region the secondary precipitates were found at the grain boundaries, which lower the corrosion resistance of the material. The grain size, the proportion and distribution of matrix /fcc and hcp/, minor phases and the some mechanical and corrosion properties are related to the heat treatment conditions. These relations are presented in photomicrographs and graphs.

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STUDY OF THE DISTRIBUTION OF ALLOYING ELEMENTS DURING SURFACE ALLOYING OF STEELS BY LASER.

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The technology of metal and alloy processing by laser enables to achieve quantitatively new utility properties of functional surfaces. The effect of laser consist in high local energy densities and extremely high cooling rates in the order of $10^5 - 10^6$ °K . sec.$^{-1}$. In dependence from conditions of processing and material type the surface is thermally afected which is a phenomenon being able to be utilized for surface hardening with materials performing phase transformations in solid state. Another possibility, studied in the present contribution, is partial surface alloying.

Besides conventional steels also PM porous steels were used for experiments. The surface was enriched with Cr and Mo by surface melting. Alloying additions were deposited on to the surface in form of either a powder fixed with organic binder or a galvanic layer. For the purpose of alloying a 1 kW laser and various working schedules were used.

In the present work technological aspects of the problem, being interesting especially with PM steels, are briefly outlined. In the mentioned steels the volume change due to porosity elimination occurs requiring the optimization of the coating layer thickness and conditions of processing. Main attention is devoted to the distribution of above mentioned alloying elements in the surface layers by EDS analysis on EDAX 9100/60 built in the microscope Tesla BS 300. This information is decisive for the control of surface properties.

X - RAY SPECTRA AND IMAGE ANALYSIS OF SUPERCONDUCTING MATERIALS

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Using Energy-dispersive spectrometer Link Systems 860-series 2, a quantitative analysis of samples of classical high temperature superconducting materials ($YBa_2Cu_3O_x$) was performed. The studied materials were prepared using typical ceramical technology. The technology allows growing of crystal of superconducting compounds, however, the superconducting material is strongly nonhomogeneous. The monhomogenity is not practically changed even after a long time of baking.

The superconducting crystals were characterized by means of the X-ray mapping. In this way, a colour distribution map was obtained for several magnifications. The linescan has been carried out over these images.

The program DIGISCAN was used for statistical evoluation of particle properties in terms of size and composition of superconducting materials and nonhomogeneous remains oxides.

The following parameters were measured : mean diameter, maximum Feret, min. Feret, mean Feret, max. diameter, orientation, area, convex. area and convex. perimeter.

CHARACTERIZATION OF METALLIZED CERAMOVITRONS WITH EPMA

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Corundum-glass mixtures are used to prepare foils, on which metallic pastes are printed, followed by a burning process to achieve a compact material. The applied temperature should be lower than 1270 K to realize conditions of "low temperature co-firing" /1/. As conductible component of the paste silver can be used /2/. The migration of the metal into the ceramovitron depends on the glass system and was investigated by the EPMA method. The combination of local point analyses, line scans, and a new developed two-dimensional measurement of the concentrations in about 2500 points yields a comprehensive characterization of typical sample areas /3,4/. The distribution of silver as the result of the firing process is visible in fig. 1 for two different combinations of metallic paste and ceramovitron.

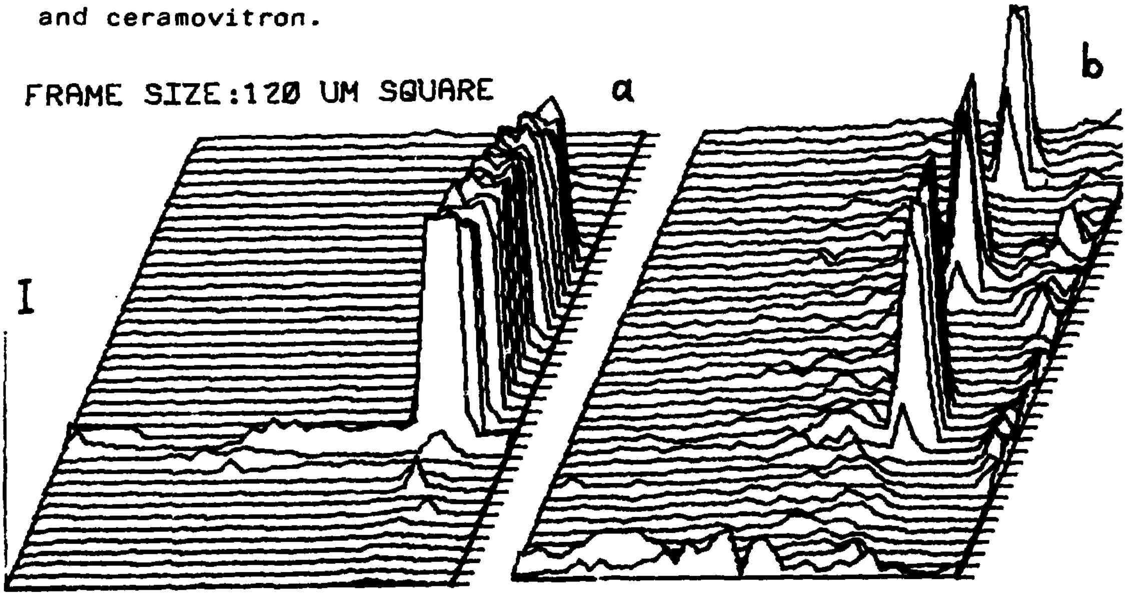

Fig. 1: Distribution of the Ag component near the interface metal/ceramovitron

a) alkali glass + silver paste 1
b) earth-alkaline glass + silver paste 2

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/4/ Sprenger, H. et al., 7. Tagung Mikrosonde, Dresden 1988

APPLICATION OF LOCAL ELECTRON MICROANALYSIS IN THE STUDY OF STRUCTURAL CHARACTERISTICS IN Ag BASE ELECTRICAL CONTACT MATERIALS

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In Ag based electrical contacts for low voltage application the attachment of the contact to the backing material seems to be one of the most important questions. Along with the state of the structure itself the attachment also affects the contact life during exploitation. Two basic problem circles with AgCdO 15, $AgSnO_2$ 15/20, AgNi electrical contacts are studied in the work :

1. Interfaces of the brazing metal with the material of the contacts as well as of the backing material were followed by the EDS methods. It turned out that an repressive interaction of melted brazing metal mainly with the backing material (Cu, resp. Cu alloy) occurs. This interaction quarantees for the good quality of contact attachment.
2. An important problem is affecting the contact surface and structure after exploitation (high temperature in the area of electric arc, dissociation of secondary phase, diffusion processes). Changes in the distribution of CdO secondary phase after exploitation were followed by means of EDS analysis. Surface and structure of some contact types after damage due to arc erosion were analysed.

References :

/ 1 / Keil, A., Merl, W.A., Vinaricky, E. : Elektrische kontakte und Ihre Werkstoffe, Springer Verlag, Berlin, 1984
/ 2 / Wörle, B., Saeger, K.E.: Pract. Metall., 22, /1985/, p.536

CHARACTERIZATION OF DIFFUSION PROCESSES IN MICROELECTRONICS BY MEANS OF THE ELECTRON-PROBE MICROANALYSIS

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Diffusion processes are of special importance in microelectronics to contact components. The compounds, in general intermetallic ones, exert negative effects on electrical and mechanical properties of the materials envolved. It is aspired to avoid these zones if it is possible, e.g. by interconnection of barriers or to reduce by appropriate material combinations.

The material pairing Cu-Sn/Pb is of great interest and form the intermetallic compounds Cu_3Sn (ε) and Cu_6Sn_5 (η) during the soldering ($T = 240°$) and tempering process ($T = 150°$).

By Ni/Cr barriers between the chip metalization material Cu and the Sn/Pb-solder these compounds can be avoided at all, whereas by defined alloying of the solders with Cu the solubility limit for Cu in Sn is reached more quickly especially during the soldering process, thus, reducing the unsoldering of Cu from the chip metalization material.

Both techniques result in more stable electrical properties of the contacts.

In the paper the quantitative characterization of the diffusion zones by means of electron-probe microanalysis is done. Additionally, the contact resistence of the system "two contacted joints between two Cu-chip metalization material with solding bases" in dependence on the diffusion process for the solding process on the one hand and for the tempering behaviour of the contacts on the other hand is determined. As basic material the LSn60-solder and the copper materials Cu-massive as well as the thick-film paste DP9923 and DP9924 were applied.

SECONDARY ELECTRON SPECTROSCOPY AT VARISTOR- AND PTCR-CERAMICS

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The behaviour of elements of ZnO-varistors and $BaTiO_3$-ptc resistors is given by the current-voltage characteristic, respectively by the temperature variation of resistance of grain boundaries between single pairs of monocrystals in a three dimensioning network of grains.

For the interpretation of the varistor- and ptcr-(positive temperature coefficient of resistivity) - effect at semiconductor- and ferroelectric ceramics it is important to know the potential distributions in microareas of electric contacted elements.

For this potential measurement at the grain boundaries we developed a contactless method by means of secondary electron (SE) spectroscopy, with a scanning electron microscope (Tesla, BS 300). We measured the SE-energy distribution with a retarding field electron spectrometer, added with an accelaration field between sample and spectrometer.

At a given lateral resolution of ~1 μm we observed an electrical potential resolution of 100 mV with a special sample stage at temperatures between RT and 500 K.

The results of our experiments are given by information about the hight of potential barriers at a grain boundaries network as a function of voltage, temperature and time loading.

We will give typical results at ZnO- and $BaTiO_3$-ceramics.

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MORPHOLOGY AND NONDESTRUCTIVE CONCENTRATION DEPTH PROFILING OF InP(100) FACE

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Scanning electron microscopy (SEM), electron microprobe analysis (EMA) and angular resolved photoelectron spectroscopy (ARXPS) have been used to morphology and composition charakterization of the InP(100) surface subjected to a series of surface treatments.

InP wafers were cut parallel to the (100) plane ($\pm$ 0,3°) from the S dopped single crystal (Tesla - VÚST) characterized by free electron carrier concentration of $5 \times 10^{18} cm^{-3}$. A mirror - like surface was obtained by mechanical polishing followed by etching in 0.4% bromine methanol solution. The final cleaning procedure and measurements were performed in VG Scientific ADES 400 angle resolved spectrometer. Surface was cleaned from possible contamination and oxide layer by sputter cleaning by an argon ion beam (3 keV, $2 \times 10^{-5} Acm^{-2}$, 300 sec.) at 150 K target temperature.

The native oxide layer on InP(100) has appeared to be inhomogenic in depth. The near surface composition is close to $InPO_4$, while in depth the oxide is more In rich. Whole oxide thickness usually achieved was 1.5 - 2.5 nm. Room temperature ion beam etching degenerates morphology of the InP(100) surface. The preferential sputtering of P results in the formation of the In globules. Ion beam etching at lower temperature has hindered the morphology degradation. ARXPS data has shown that P is again preferentially sputtered but no globules were observed by SEM. Such surface is free from contamination and oxide. Clean and atomically ordered surface of InP(100) 4 x 2 mm has been obtained after flash at 300°C. Heat treatment to higher temperature has caused formation of globules consisting of In, as seen by an EMA.

EDS ANALYSIS OF SUPERCONDUCTING La-Ba-Cu OXIDE

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Recently have been observed an apparent superconducting transition in La-Ba-Cu oxide with the resistive transition beginning at ~ 30 K. This phenomenon has caused a considerable interest in the study of the structure of such materials.

We have tried to determine the existing phases in the system La-Ba-Cu-oxide where the Ca atoms were substituted for Ba. The structure analysis was performed using metallography, EDS and XRD methods. The samples were prepared by solid state reaction of oxides.

EDS analysis enabled to determine the value of the ratio between La:Ca:Cu in the phases that were present in the structure, to identify the phase of K_2NiF_4 type and to find the connection between the composition and the temperature behaviour of electrical resistivity of samples.

The EDS analysis is useful to use as effective method for study of phase equilibrium in the systems that show the high temperature superconductivity properties.

MONTE-CARLO CALCULATION OF ELECTRON TRANSMISSION THROUGH THE THIN FILM - BIOLOGICAL APLICATION

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Monte Carlo method is widely used for a simulation of physical processes, which are not fully theoretically described for their complexity. Interaction of electron (energy 10^4 - - 10^5 eV) should be studied for information on the angular and energy distribution of transmitted and backscattered electrons as well as for local and energy distribution of emitted X-ray photons.

Some remarks on the problem of transmitted and backscattered electrons were given in our previous works (1, 2). Our recent results are concerned firstly on the depth distribution of X-ray production and lateral resolution of X-ray mapping and secondly on peak-to-background ratio calculation and its comparison with experiment for biological samples.

Because the efficiency of X-ray emission is very low, we supposed in our calculation the photon was created at every scattering with energy loss; finally, the intensity ratio for K, L, M lines of characteristic radiation and continuum one was found by counting together of all producted photons. The current electron energy was used in calculation of photon emission probability. For comparison with experimental results, we supposed the isotropic distribution of photon directions; the X-ray absorbtion in thin film was neglected, too.

The histograms of energy-angular distribution of transmitted electrons, the beam broadening profiles with their X-ray map and relative intensities of emitted X-ray will be presented.

References:

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SEDIMENTARY ROCKS ELECTRON BEAM STUDIES

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The presentation deals with the analysis of sedimentary rocks by means of electron beam. It focuses on 2 basic areas: (a) the features and elementary composition of individual sand grains and (b) the elementary characteristics of the matrix.

In the analysis of the quartz sand grains new interpretation of the surface structure deformation was arrived at. In some instances it seems that the steps on the guartz sand grains surface structure were not caused solely by their genetical conditions, but by the geomechanical deformations as well.

The influence of the geomechanical forces on the changes in the chemical composition and structural characteristics of the matrix was examined, too.

The investigation was based upon scanning electron microscopy (SEM) and electron microanalysis (EMA) methods. Jeol JSM 35 CF with wavelength dispersive spectrometer and Link Systems 860 energy dispersive microanalyser were applied.

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THE STUDY OF CHEMICAL COMPOSITION AND INTERNAL STRUCTURES OF DEEP-SEA MANGANESE NODULES

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Problems of deep-sea manganese nodules have concentrated great deal of interest during the last, two decades. Our work presents the results and interpretation of the microanalysis of a group of samples carried out with the EDAX-PV-9100 system. In order to choose most representative points for microanalysis, the samples of manganese nodules have been also studied with the Scanning Electron Microscope JSM-840. This enabled the evaluation of their internal structures and textures. Studied nodules have been described after relation between number of cores and final shape of the nodules, as well as on the basis of textural relation between the core and slope. Microlayers, which have been documented with the BEI method /back scattered electron image/ show typical structures. The layers with botryoidal structure have been present more often than oxidic layers with globular and especially laminar structure. SEM photomicrographs show also systems of transversal or parallel cracks, which reflect the growth succession of studied nodules. On the basis of Mn/Fe ratio the nodules and/or oxidic layers have been divided into four groups. In all cases the positive correlation Mn with Ni and Cu have been confirmed. In cavities and cores of the studied nodules, the fragments of authigenic minerals and basaltic rock have been identificated.

THE USE OF EDS-ANALYSIS FOR STUDYING THE MECHANISM OF LEACHING OF CHALCOPYRITE

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The leaching of chalcopyrite with iron/III/ sulphate in acid medium is governed by the following equation

$$CuFeS_2 + 2Fe_2/SO_4/_3 \longrightarrow CuSO_4 + 5FeSO_4 + 2S \qquad 1.$$

The mechanism of reaction 1. is complicated and no common view about the rate determining step exists in literature. The classic identifikation methods for studying of the mechanism of leaching are chemical analysis and X-ray phase analysis. White the chemical analysis enables us to estimate the distribution of copper and iron in extract liquor, the X-ray metod gives information about the presence of crystalline reaction products. The analysis of the amorphous products, e. g. elementary sulphur arisen in reaction 1., is frequently problematic. A contribution in this line is the EDS method which was for the first time used in a semiquantitative variant for studying reaction 1.

As for the EDS analysis of the samples investigated in powdery form, the conditions of recording the energy spectra were optimized by a series of preliminary measurements. Ten analyses were carried out with each sample. The obtained EDS spectra were evaluted by the semiquantitative analysis without any standard and the results were processed statistically.

We have revealed in this study that the rate of transfer of copper and iron is dependent on the degree of development of reaction 1. Provided it holds for the time of leaching $t < 15$ min, copper is preferentially transferred to the extract liquor but for $t > 15$ min the solution is enriched with iron. In higher reaction stage /$t \geq 60$ min/ a stationary state is attained which might be a consequence of the inhibitory deposit of elementary sulphur on the surface of reacting chalkopyrite. The results are consistent with literary data about the formation of intermediary sulphides of copper in the course of leaching of chalcopyrite.

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EPMA INVESTIGATIONS ON HUMAN BONE TISSUE

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In patients with chronic renal failure occur bone alterations, in which pathological inclusions of aluminium in the bone tissue are discussed /1,2/. The microscopic proof of this element and its topographic demonstration in the bone is possible by specific staining methods, but quantitative analytic results were not obtainable up to now /2/.

By use of the EPMA method on 20 μm thick bone sections, which were obtained by iliac crest biopsies, we tried both the localization and the quantitative estimation of the included aluminium. In addition to point analyses and line scans a computer controlled multi step-scan measuring method was developed to make visible the distribution even of small amounts of elements. As a result the deposition of aluminium in the contact zone of bone and osteoid (so-called mineralization front) can be veryfied microanalytically. There were found semi-quantitatively more than 1.0 wt. percent of aluminium. The completely mineralized bone tissue contained up to 0.3 percent Al in this case.

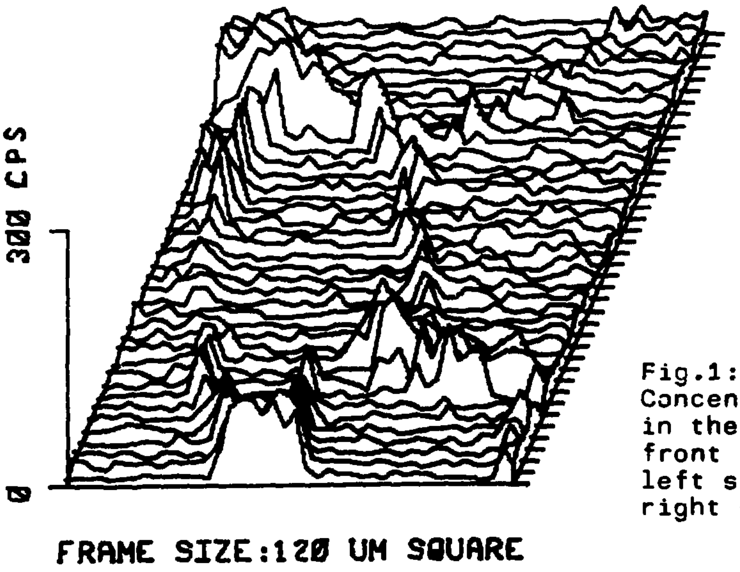

Fig.1:
Concentration of Al
in the mineralization
front
left s.: osteoid
right s.: mineral. bone

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/2/ Delling, G. et al. Nieren- und Hochdruckkrankheiten 12(1983)

STUDY OF CRYSTAL STRUCTURES OF BIOLOGICAL FLUIDS

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To specify diseases of human organism, our Health Service successfully uses various diagnostic methods based on investigation of humors and excrements. Besides standard biochemical methods, a new approach was established for diagnosing physiology and pathology of humors and excrements. The principle of the method is that properties of crystal-forming solutions are undergoing changes under special conditions due to effects of the biological substrates. Thus, urine can be examined by this method, as well as blood serum, cerebrospinal fluid, saliva and other biological fluids, or extracts from tissues.

The principle of the crystallographic method lies in selecting an adequate crystal-forming matter. Of them, NaCl is the best, with regular cubic crystals. Solution of a crystal-forming matter which is mixed with a substrate is prepared in destilled water up to a value of 1%. Growing crystals from the mixed crystal-forming solution and substrate in ratio 1 : 1 are developing on a support with a defined background, at a constant temperature and in a dust-free medium. After, the samples are evaluated in Scanning Electron Microscope and X-ray Microanalyzer.

To illustrate this, we present a crystallization of blood serum, cerebrospinal fluid, urine and saliva. In case of blood serum, crystallograms sampled for a healthy individual evidenced elongated crystals of a dendritic type, with some crystallization centers and regular crystallization. Contrary to the above, we present crystallograms of all malignant diseases as cardie, pulmona and vesicae urinae. A typical dendritic crystal structure is nearly absent, being replaced by inexpressive branch-shaped crystals, or by combined dendritic and branch-shaped crystals.

Referred to the fact that a process of crystallization is influenced above all by properties of an applied biological substrate, the method of X-ray microanalyses seems to be suitable enough to determine a quantity of elements in a sample.

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X-ray Spectral Analysis

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THE COORDINATION GEOMETRY, BOND LENGHTS AND MODEL CALCULATIONS OF XANES

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Abstract not delivered

THE CHANGES IN THE VALENCE BAND IN Cu_2O, CuO AND $YBa_2Cu_3O_{7-x}$ DETERMINED BY THE X-RAY EMISSION

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(YBaCu)-oxides form a new class of materials that show superconductivity above liquid nitrogen temperature [1]. The superconducting mechanism is not easily understood yet. Therefore a detailed knowledge of the valence band structure is of great importance.

The Cu-atoms seem to play the dominant role for the superconductivity of these materials. Hence an investigation of the valence states localized on the Cu-atom should be very informative. For such purpose x-ray emission bands (transitions from the valence states to the core hole) are most appropriate.

We studied the $CuK\beta_{2,5}$ emission band (transition from the valence band to the 1s hole). The dipole transition $1s \rightarrow (O2p,2s)_p$ gives the emission band of low intensity because these states are predominantly localized on the O-atom. As a result of the partial sharing of the Cu3d states in the bond the additional states $(Cu3d)_p$ are formed. They give rise to another emission band corresponding to the dipole transition $1s \rightarrow (Cu3d)_p$. Its intensity is comparable with the band of the $(O2p,2s)_p$-origin. Hence even changes of the Cu3d-states may be clearly visible in the $CuK\beta_{2,5}$ emission band.

The evolution of the x-ray $CuK\beta_{2,5}$ emission band in the studied oxides is given. Passing from Cu_2O to CuO and (YBaCu)-oxide the amount of the $(Cu3d)_p$-states in the valence band increases. Our measurements proved that the participation of the Cu3d electrons in the bond Cu-O is definitely higher in $YBa_2Cu_3O_{7-x}$ in comparison with CuO.

[1] A. Knurana, Phys. Today 40 (No4), 17 (1987)

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THE X-RAY K-BANDS OF GERMANIUM IN CHALCOGENIDE GLASSES DOPED BY Bi OR Sb

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The chalcogenide glasses usually show p-type conduction. Recently, it has been reported e.g. [1] that Bi-doped chalcogenide glasses exhibit n-type conduction. There exist different models which explain this unusual feature. Therefore it seems to be informative to study the electronic structure of these materials.

We measured the x-ray K-emission and absorption bands of germanium in two amorphous systems $(GeS_2)_x(Bi_2S_3)_{1-x}$ and $(GeS_2)_x(Sb_2S_3)_{1-x}$. In the former system (Bi) strong interaction among the components is supposed; the latter (Sb) is assumed to be nearly ideal solution. The shifts of the Ge K-emission and absorption edges measured by us do not correspond to the changes of the optical gap given in [1]. Our results are compared with the measurements of the K-absorption edges in analogical systems $Ge_{22}Se_{88}X$ (X=Bi, Sb) [2].

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A CHOICE OF SPECTROSCOPIC SCHEME IN X-RAY PLASMA DIAGNOSTICS

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During the past decade, many high-power laser systems have become available enabling to irradiate solid targets with power above 10 TW/cm^2. Under these conditions, the high temperature and dense plasma is created, which emanates very intense and short x-ray pulses. The instant flux of soft monochromatic x-rays is extremly high, at present the laser generated plasma is the brightest of all laboratory x-ray sources including synchrotrone. The conversion efficiency of laser radiation into 1 keV x-rays may exceed tens per cent, thus enabling numerous application (e.g. real time kinetic studies of phenomena in solids). In accordance with equilibrium states collisional models, x-ray line and continuum emission is closely connected with the spatial and temporal evolution of the values of electron temperature, density and ionization states of participating atoms /1/. The measurement of x-ray spectral output is therefore a basic tool to optimizing the plasma sources and to understanding the phenomena occuring in plasmas. In recent years, many x-ray diagnostic methods were developed /2/. The aim of this paper is to discuss the choice of spectroscopic method in the spectral region above 500 eV. The instruments used to this purpose are usually based on fixed crystal analyzers /3/, the parameters of spectrometer depend on required spectral range, dispersion, luminosity, imaging properties and resolving power. As a rule, the instrumental effects cannot be deduced from simple analytical formulae; therefore we have developed the ray tracing codes, on the basis of which all the necessary quantities may be determined and the design of spectrometer optimized. The principles of ray tracing are explained and the structure of codes for flat, cylindrically and spherically bent crystal spectrometers is described. In contrast to standard ray tracing codes /4/, the two dimensional source and the real shape of single crystal diffraction pattern in dependence on the radius of curvature /5/ are taken into account. The geometric factors may be changed in broad limit, thus enabling to calculate the influence of alignment on the main characteristics (i.e. the resolution and luminosity) of the apparatus. The results of calculations performed on Siemens 7536 computer are presented. Finally, the properties of Johann, von Hamos type and sperically bent spectrographs are compared with those of flat crystal spectrometer.

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/2/ V.A. Boiko et al.: J. Sov. Laser Res. 6(1985), 85.
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PS 37

COMPARISON OF THE OES AND XRF METHODS FOR THE DETERMINATION OF MINOR ELEMENTS IN STEELS

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In spectrochemical laboratories of Třinec Iron and Steel Works we analyse alloyed steels including minor elements on the optical emission spectrometer ARL 31 000 C and on the X-ray fluorescence spectrometer ARL 8680.

ARL 31 000 C is a simultaneous spectrometer with the argon spark stand. Meassuring conditions were: prespark 15 seconds (55/uF, 20/uH, 500 V, 100 Hz), analysis 10 seconds (10/uF, 20/uH, 400 V, 100 Hz, 2.5 Ohm).

ARL 8680 is simultaneously - sequential XRF spectrometer, equiped with 20 monochromators and programable goniometer. Conditions for X-ray tube (OEG 76 H with Rh target) were 60 kV, 45 mA. Analytical lines were NbKα, AsKβ, PbLβ, ZrKα, TaLα, CeLα, dispersing crystal was LiF$_{200}$. Nb and As were analysed on monochromators with Xe sealed detectors, the rest of elements was meassured on the goniometer. For Pb, Zr, Zn and Ta was used scintilation detector, for Ce was used flow proportional detector.

Limits of detection, calculated as 3 standard deviations obtained by 20 meassurements of the standard ČKD 162 B, are compared in the following table.

ELEMENT		Nb	As	Sn	B	Pb	Zr
LOD (%)	OES	0.002	0.003	0.002	0.0005	0.003	0.003
	XRF	0.001	0.006	-	-	0.003	0.001

		Sb	Zn	Ta	Ce
LOD (%)	OES	0.01	-	0.004	0.005
	XRF	-	0.002	0.006	0.005

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SAMPLE PREPARING METHODS FOR XRF ANALYSIS DUE TO THE ITZ-1 BEAD MACHINE

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Výzkumný a zkušební ústav NHKG, Ostrava

Abstract not delivered

X-RAY FLUORESCENT SPECTROMETER APPLICATION FOR THE INVESTIGATION OF MOTOR-CAR PARTS.

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Designing of new motor-cars and modernizing of the alredy existing ones calls for verification of constructional and technological assumptions that underlie them.

The conditions in which the vehicles are exploited and which are often difficult to be forseen cause loss of serviceability of parts and assemblies.This makes it necessary to determine the causes of a failure.

The most commonly used durability tests are but a part pf the whole range of verification.tests.At our university there has been developed a method of testing and determining the reasons of premature vehicle parts wear and a specialized testing equipment has been applied.The investigations carried out in connection with the national economy needs, enabled the application of substitute materials in vehicles construction and of alternative kinds of fuel to energize the vehicles.

Parts of domestic and imported motor-cars and tractors, that were defined as prematurely worn,needing regeneration or as requizing spare parts,have been subjected to the macroscopic as well as microscopic tests and to the chemical analysis of the surface layer.This tests were carried out by means of the VRA-2 X-ray fluorescent spectrometer and CAMECA MS-46 X-ray microprobe.

The analysis of the obtained results has proved that the dominant type of wear of the tested parts was the quasi-abrasive wear and another type was the corrosive wear.

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DETERMINATION OF MAJOR ELEMENTS IN LIMESTONES BY WAVELENGTH DISPERSIVE XRF

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A method for determination of ten oxides /Si, Ti, Al, Fe, Mn, Ca, Mg, Na, K and P/ in limestones is described.

The sample mass taken for fusion is adjusted according its loss of ignition and bivalent iron to keep the ignited sample : flux ratio equal to 1:5. The sample is fused with a mixture of $Li_2B_4O_7$ and $LiNO_3$ in a Pt-Au crucible for 10 min at 1200^o and the melt is poured into a preheated /500^o/ Pt-Au dish to form a glass disc.

Conditions found experimentally for determination of the ten elements include also suitable angles for background measurement. For the evaluation of ten oxides the method of internal reference as descriebed by de Jong, Müller : Glasstech. Ber. 44,506 /1971/ was used.

Concentrations of the determined oxides are expressed relatively to calcium concentration in the sample, i.e. the intensity ratio "element/calcium" is plotted against the concentration ratio "element/calcium". The actual concentrations of elements can be calculated because the sum of the analysed oxides is known /it varies only slightly around a known average/. Calibration curves of the elements are thus independent of measuring conditions and quality of the borax glass disc surface. The assumption that interelement effects in limestones are negligible was confirmed.

The calibration graphs were made using ten reference samples of different composition. The results compared with those obtained by classical analysis were found in good agreement.

THE ANALYSIS OF BRONZE HOARDS FROM HOŘOVIČKY, RAKOVNÍK DISTRICT, CZECHOSLOVAKIA

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Accidentally discovered bronze hoards (78 ingot torques) in Hořovičky, Rakovník District, Czechoslovakia, were analysed by means of dispersive X-ray fluorescent analysis. The hoards belong to the Únětice culture (early bronze age), approximately 2.000 years B. C. The site of discovery is significant by the fact that nearby were identified grave place, settlement and metal processing feature, i. e. all fundamental components of archaeological cultures with the exception of hill-fort.

The hoards differ in shape, form and weight. The aim of this work was to determine the metal composition of every item. Combining all the available data we discuss the observed differences as well as interpretation of composition and origin of the hoards.

POSTERS PS 46 - PS 62
PS 101

Mössbauer Spectrometry

PS 46

A CRITERION FOR THE EFFICIENCY OF THE MEASUREMENT OF MÖSSBAUER SPECTRA

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The problem of maximum speed of collecting information becomes important when either small intensity of the Mössbauer resonance line, or very low countrates are encountered. In these cases, a careful optimization of the measuring process is reasonable. Therefore, a criterion is necessary which would provide a measure of quality of the information collecting process. Such a measure must involve the countrate as well as the intensity of the resonance line.

A criterion was found by means of which the signal-to-noise ratio can be derived from the measured Mössbauer spectra. Using the Poisson's law of distribution, the signal-to-noise ratio can be defined as a reciprocal value of the relative error per time unit

$$R = \frac{1}{\sigma_{\varepsilon} t_{\infty}} = \frac{\varepsilon}{\sigma_{\varepsilon} t_{\infty}}$$

which means the rate of decrease of the relative error. Two forms of the formula are derived, one for the constant acceleration, the other for the constant velocity (ON-OFF) modes of measurement. The maximum value of R corresponds to the optimal setup of the measurement.

In this way, the performance of all elements which participate on the measuring of the Mössbauer spectra can be estimated (e.g. source, geometry of the measurement, resonant absorber, detector, single-channel analyzer, etc.). One of the most important parameters which significantly influences the efficiency of the measurement is the thickness of the resonant absorber.

Several series of measurements with different resonant absorbers were carried out using this criterion and the optimum thicknesses were determined. For the ^{119}Sn resonance, the optimum thickness of the palladium X-ray filter was determined as well.

A DENSITY MATRIX APPROACH TO THE GOLDANSKII-KARYAGIN EFFECT

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The influence of the recoilless fraction anisotropy on absorption Mössbauer spectra has been analyzed using a density matrix formalism. An Edgeworth expansion has been adopted to describe the recoilless fraction in a model-free fashion. A detailed analysis is given for the relationships between Edgeworth tensors and density matrix elements. Some numerical examples are analyzed in detail and they indicate that quartic anisotropy can be observed by the Mössbauer effect in quadrupolarly dominated transitions. A software package, which is able to deal with the problem in a general way, has been developed and implemented. It is available to interested users. Details of this work are to be published elsewhere.

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DETERMINATION OF THE MAGNETIC TEXTURE OF Fe-Si SHEETS BY MEANS OF MÖSSBAUER SPECTROSCOPY

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The texture is one of the most important parameter of the quality of Fe-Si electrotechnical steel sheets. However, its description is reported mostly by the X-ray pole figures only and the magnetic texture is deduced from the known magnetic anisotropy. Because of complexity of real materials, a direct measurement of the orientation of the magnetic moments in the sheets will be very useful. The Mössbauer spectroscopy can yield this information as the intensities of the lines in spectra of the ferromagnetic materials depends on the angle between the magnetic moment and the direction of the photon propagation. In practice where a backscattering geometry is used a convolution of the angular distribution of both photons and magnetic moments directions must be taken into account. The comparison of the theoretical analysis with the experimental results on the oriented and non-oriented Fe-Si sheets shows that the direction of magnetic moment agree with the X-ray determined texture, but the angle resolution is poor. To improve the resolution a narrower photon beam must be used. It means, that the strong Mössbauer sources are necessary for practical measurements when a good angle resolution is requested.

MÖSSBAUER SPECTROSCOPY OF THE DEFORMED CARBON- AND NITROGENE- STEELS

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Mossbauer spectroscopy study showed without any hesitations partial decomposition of cementite (Fe_3C) and nitrides (Fe_4N and $Fe_{2+x}N$) at cold plastic deformation of steels. Different degrees of cementite and nitrides decomposition has been fixed.

At annealing of the cold-deformed steel cementite partially restores and graphite is partially formed. The degree of nitride restoration is near 100%.

Thermodynamics and carbide- and nitride phase decomposition mechanism is discoussing on the basis of study of the persipitated carbide and nitrides, and effect of the alloying elements on the decomposition degree and analysis of the interaction energies of carbon and nitrogene atoms with dislocations.

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MÖSSBAUER SPECTROSCOPY OF LASER SURFACE ALLOYED STEEL

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One of recently developed techniques enabling the deposition of coatings protecting steel against corrosion or abrasion consists in surface alloying by laser radiation. A set of samples was prepared by surface alloying of steel with Ni and Al. Prior to laser irradiation, several types of coatings composed of Ni-Al alloys were deposited on low-carbon steel by thermal spraying. Afterwards, the samples were irradiated by a continuous CO_2-laser. This resulted in melting of the coating and underlying steel to a certain depth and in the formation of an alloyed layer. The energy dispersive X-ray microanalysis was used for the determination of concentration profiles of the alloying elements. The phase analysis was based on Mössbauer scattering spectroscopy and on X-ray diffraction. Both methods give similar results for phases, the content of which in the alloyed layer is high. For minor phases, some discrepancies appear due to differing detection limits of both methods. Layers poor in Al are composed mainly of a ferromagnetic Fe-Ni phase. For higher Al concentration, the predominating phase is paramagnetic Ni-Al with a low Fe content. The Mössbauer analysis involved relatively thin surface regions of alloyed layers. However, with respect to a sufficiently uniform distribution of alloying elements, the results can be taken for typical of the whole volume of the alloyed layers.

LASER IMPLANTATION OF IRON INTO HIGH-MELTING MATERIALS

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The paper presents the results of studying the structure of surface layers formed under laser irradiation of a thin-film coating (~100 nm) ^{57}Fe deposited on massive substrates from Ti, Nb, Zr and Ta.

The surface layers of samples were studied by the X-ray diffraction and Mössbauer electron spectroscopy. Secondary electrons were registered with a gas-flow He-CH$_4$ detector. The radioactive isotope ^{57}Fe in Cr matrix was used as a resonance irradiation source.

The comparison of X-ray spectroscopy and Mössbauer data makes it possible to obtain a qualitative picture of the layer-by-layer element distribution. Laser treatment was performed by light pulses of YAG : Nd - laser (the pulse duration $\tau_1 = 2.5$ ms, the energy $E_1 = 0.5 \div 0.7$ J, the irradiation wave length $\lambda_1 = 1.06$ mcm).

It is concluded that under pulse laser irradiation the alloying of Fe thin film coatings with a massive substrate occurs. A complicated multiphase structure with a preferred arrangement near the surface of the most low-melting phases is formed in the Ti-Fe, Fe-Nb, Fe-Zr and Fe-Ta systems. In the Fe-Ta system the Fe-Ta amorphous alloy layers are formed under the above treatment.

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REDISTRIBUTION OF ELEMENTS IN METAL SURFACE LAYERS DURING LASER TREATMENT AND ELECTROSPARKING

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High cooling rates of a metal after laser and electro-sparking alloying make it possible to fix various metastable states of treated surfaces. The analysis of such states is of particular interest as the latter can possess some properties differing markedly from those obtained under equilibrium conditions.

The surface layers formed due to pulse laser treatment (τ_i = 2.5 ms, $E_i \approx$ 0.5-0.7 J, λ_i = 1.06 mcm), and electrosparking alloying by iron anode ($\tau_{treat.}$ = 60 s, $E_i \approx$ 0.9 J) of copper covered with ^{57}Fe alloy up to 100 nm thick were studied by the Mössbauer electron spectroscopy, radioactive isotopes, etc.

After electrosparking alloying, the γ-Fe regions 10 to 20 nm in size as well as the α-Fe regions being in a supermagnetic state were found. Moreover, in the above layers we found up to 11% of oxygen but Fe oxides were absent.

Under the conditions of laser alloying, a phase with the least melting temperature for the Fe-Cu system is formed at the surface. Similar results were also observed in the case of electrosparking alloying. The above phenomenon is indicative of the fact that the electrosparking alloying and laser treatment used in the present paper sometimes have the same influence on metals.

PHASE ANALYSIS OF WELDING AEROSOLS USING MÖSSBAUER SPECTROSCOPY

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Welding aerosols (solid phase of welding fumes) is an inhomogenous mixture which according to the character of base and filler metals can contain large number of phases. It has been shown that beside the mass spectrometry, X-ray analysis, neutron activation analysis the Mössbauer spectroscopy plays important role in the determination of the phase composition of welding aerosols.

We have studied various types of welding aerosols collected during different welding processes and different groups of materials (mild steel, stainless steel, special steel for nuclear reactors etc.).

From the parameters of Mössbauer spectra the following general conclusions can be drawn : a main magnetic component of welding fumes is substituted magnetite $Fe_{3-x}M_xO_4$ where x is the degree of substitution and M represents substituents (Co, Cr, Mn, Mo, Ni, etc). A computer analysis of the spectra shows that the degree of substitution varies from x=0,3 to x=1,0. Large widths of resonant lines are caused by unequal substitution of various ions. Some samples contain maghemite or small amount of hematite too. The MIG/MS and MIG/SS welding fumes contain approximately 7% α-Fe and 12% of γ-Fe respectively. In all spectra paramagnetic components occur. They can correspond to the high substituted magnetite ($x \geqq 1$) or to other compouds (minerals, amorphous componets). Similar doublets can signify occurence of so-called superparamagnetic particles, however. The relative amount of iron in paramagnetic components varies from 20 to 100%.

MÖSSBAUER SPECTROSCOPY STUDY OF Ba - HEXAGONAL FERRITES PREPARED BY A WET METHOD

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Ba-hexagonal ferrites have been the subject of numerous investigations in the past especially with regard to their magnetic properties. The firing and milling procedures are commonly used to prepare a ferrite powder. On the other hand there exist several methods avoiding the milling process.

We have employed the Mössbauer spectroscopy, x-ray analysis and magnetic measurements to study the process of formations of $BaFe_{12}O_{19}$ ferrites prepared by a wet method. The solution of iron nitrate, barium hydrooxide and citric acid were mixed to obtain stoichiometric ratio of Ba and Fe for the hexaferrite formation.

In order to optimalize the whole process (dehydration, decomposition, refiering) the products of all steps of the preparation were analyzed using mainly Mössbauer spectroscopy. We have observed that the beginning of the hexagonal phase formation is at the temperature 600°C. After heating up to 950°C for 3 hours a solid powder was formed. In the Mössbauer spectrum of this powder we have identified such number of lines which give evidence for 5 nonequivalent crystalographic position of iron ions denoted as $4f_2$, 2a, $4f_1$, 12k and 2b. Amount of the iron cations in each possition corresponds with the stoichiometric Ba-hexaferrite. This cation distribution was obtain after treatment in a 50% aqueous solution of HCl for 15 minutes. Such treatment causes the disappearing of other phases (monoferrite) which are dissolved in HCl.

Our conclusion were proved also by x-ray analysis.

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MÖSSBAUER SPECTROSCOPY OF IRON PHOSPHIDES

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The application of phosphorus ionic implantation for obtaining the required properties of materials finds extensive use in technology. The present work deals with the study of Fe and P compounds.

The synthesis of Fe_3P, Fe_2P and FeP was performed during two days by a slow temperature increase up to 1223 K with a subsequent annealing at that temperature. The Fe_3P compound was annealed during 30 days to avoid overcooling, and Fe_2P and FeP were annealed during 7 days. The FeP_2 compound was obtained at 1073 K (the temperature was raising during 5 days to that point). After annealing the samples were grinded in an agate mortar, repressed in briquettes and annealed in sealed vacuum tubes for homogenization during 14 days at the same temperatures. Thereupon the product was analyzed for phosphorus and iron.

The investigations were performed with the Mössbauer spectrometer operating under uniform acceleration in the geometry of absorption at 300 K and 65 K.

We have obtained the spectra which can be used for calibrating Fe spectra after ionic implantation by P ions.

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APPLICATION OF ATOMIC ABSORPTION SPECTROMETRY AND MÖSSBAUER SPECTROSCOPY FOR ANALYSIS OF IMPURITIES IN SYNTHETIC DIAMONDS

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When producing synthetic diamonds an interaction of graphite with the metal matrix occurs during the synthesis and this is the source of impurities present in the synthesis product - diamond. As the amounts of impurities are not negligible and influence the final properties of the product, namely strength and heat resistance, the experimental system was examined, in which impurities amounts /Fe,Ni,Co,Mn/, their distribution and form of their presence were determined.

The synthetic diamonds were divided into three groups by separation in the magnetic field of various strength. These diamond groups were then analysed by AAS, IAA, optical microscopy, electron microscopy and a static method for determining individual strength of grains. The group with maximum amount of ferromagnetics was analysed by Mössbauer spectroscopy in order to determine the form, in which the present impurity is bound in the diamond crystal. Also homogeneity of impurities distribution was examined by this method and the results were compared with microscopic observations.

By the experiment following results were obtained:

1/ The amounts of impurities over 1 wt.% are present in the diamond as interstitially distributed inclusions.

2/ 95 % of the present inclusions are formed by a metallic ferromagnetic phase, 5 % of impurities are present in the form of a paramagnetic phase, probably carbide.

3/ Homogeneity interpretation of inclusions and crystal symmetry by Mössbauer spectroscopy and of values ΔE_Q, $\bar{B}ef$ and Bef is in accordance with microscopic observations.

RELAXATION OF AMORPHOUS ALLOYS BY MÖSSBAUER SPECTROSCOPY

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Mössbauer spectroscopy, commonly used for investigation of the crystallization of amorphous alloys, will be introduced as a method suitable also for studying the relaxation processes using its sensitivity to the local structural and magnetic changes. The most remarkable effects of low-temperature isothermal annealing of the Fe-B-based amorphous alloys exhibit the average hyperfine induction, B_{eff}, and its average direction, given by the area ratio of the 1st and 2nd lines, R, in the ^{57}Fe Zeeman sextuplet.

Transmission Mössbauer measurements were made on the $Fe_{40}Ni_{40}B_{20}$, $Fe_{70}Co_{10}B_{20}$ and $Co_{66}Fe_{5}Cr_{7}Si_{8}B_{14}$ ribbons originating from the Institute of Physics, Slovak Academy of Sciences, Bratislava. Several sets of room-temperature measurements were made during interrupted isothermal annealing runs between 150--250 °C in the logarithmic time scale.

In all cases, monotonous increase of B_{eff} was observed, while R varied in a more complicated manner. Usually two stages of exponential relaxation processes were found. From the temperature dependence of thus determined relaxation times, activation enthalpy of the pertinent mechanism was calculated. E.g., for the $Fe_{40}Ni_{40}B_{20}$ amorphous alloy, the activation enthalpy of the fastest process is ca 170 ± 10 kJ/mole well corresponding to the vacancy activation in the crystalline fcc Fe-Ni alloys. It can hence be supposed that the first relaxation stage reflects the quenched-in pseudovacancy annihilation, i.e., the free volume shrinking, followed by slower chemical short-range order changes.

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THE ROLE OF SURFACE IN THE CRYSTALLIZATION OF THE AMORPHOUS $Fe_{70}Co_{10}B_{20}$ ALLOY

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In this work, a comparison of surface and bulk crystallization of the amorphous alloy $Fe_{70}Co_{10}B_{20}$ is reported. The alloy, kindly provided by Ing.P.Duhaj, CSc. (Institute of Physics of the Electro-Physical Research Centre, Slovakian Academy of Sciences, Bratislava) was prepared by melt spinning technique. The alloy was studied in the as-quenched state and at two stages after annealings corresponding to the start and end of crystallization, the last two determined from the isothermic resistometric curve taken at the temperature of 647 K. The ribbon surface was investigated by means of optical microscopy (OM), scanning electron microscopy (SEM) and conversion electron Mössbauer spectroscopy (CEMS). For observations of the bulk transmission Mössbauer spectroscopy as well as OM and SEM of cross-sections of samples were used.

The crystallization of the bulk was indicated only after the last annealing. On the other hand, the surface crystallization was detected after the first annealing. Precipitated particles were observed on the surface of the sample in this stage by the OM and SEM. Their distribution on both the contact and free sides of the ribbon is non-uniform, but differently. The determination of depth profile of these particles at the sample cross-section has not been successful yet. The CEMS of both sides of the ribbon in this stage shows about 40 % crystalline α-Fe-Co phase whereas no borides were distinguished in the rest.

CRYSTALLIZATION OF IRON-RICH METALLIC GLASSES OWING TO THE NEUTRON IRRADIATION

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Amorphous metallic $Fe_xNi_{80-x}B_{20}$ /x=40,50,60,70/ alloys were studied by means of Mössbauer spectroscopy. The samples were irradiated in a nuclear reactor channel to the fluence range from 10^{14} to 10^{19} $n.cm^{-2}$.

Familiar six-line patterns of broad and overlapped dips were observed up to the fluence of 10^{16} $n.cm^{-2}$ for the whole concetration range. However, crystallization occured at the fluence of 10^{17} $n.cm^{-2}$. The process of crystallization can be monitored by means of the shape of a Mössbauer spectrum and hence individual crystallization phases can be determined. There is a direct relation between the degree of crystallization and the irradiation fluence. From the point of view of of composition of $Fe_xNi_{80-x}B_{20}$ glassy alloy one can conclude that decreasing the Fe content lowers the degree of crystallization. On the other hand, high Ni content in Fe/Ni-B amorphous system improves its resistance against neutron irradiation damage with respect to the crystallization.

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CONTRIBUTION TO THE FITTING MODEL FOR MÖSSBAUER SPECTRA OF METALLIC GLASSES

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Mössbauer spectra of iron-rich metallic glasses exhibit a typical Zeeman-split pattern which consists of six broad and somewhat overlapped lines. The line-broadening is a consequence of the variation of hyperfine field, isomer shift and electric field gradient at different iron nuclear sites of amorphous alloys.

Mössbauer spectrum of amorphous metallic $Fe_{83}B_{17}$ alloy was approximated by means of six broadened lines with the same mutual line position relations as those of -Fe. It has been shown by means of the results of the DISPA lineshape analysis that each spectral peak is broadened owing to a sum of Lorentzian lines weighted by a Gaussian distribution in the peak position. This model represents a Gaussian distribution of various environments of resonant atoms in amorphous metal.

An observed asymmetry in Mössbauer spectrum of $Fe_{83}B_{17}$ due to correlations among hyperfine parameters leads to non-equal line widths and intensities of the individual fitted lines.

MÖSSBAUER INVESTIGATIONS ON THE PREPARATION OF M-TYPE HEXAFERRITE PARTICLES BY THE GLASS CRYSTALLIZATION METHOD

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The individual steps of the preparation of M-type Ba-hexaferrite particles by the glass crystallization method were studied by means of Mössbauer spectroscopy. As starting materials three different compositions of the system Fe_2O_3-BaO-B_2O_3 were used. The amorphous base materials were prepared by the twin roller quenching method. In these materials Fe^{3+} ions occupy both the tetrahedral and the octahedral sites in the glassy network. At high annealing temperatures not only the crystalline Ba-hexaferrite phase, but also an amount of approximately 16% of glassy phase can be found. The Fe^{3+} content at octahedral sites in the glassy phase rises from about 25% at an annealing temperature of 300 °C to about 70 to 90% in annealing above 780 °C. Very small barium hexaferrite particles are formed at low annealing temperatures which show a superparamagnetic behaviour. The magnetic behaviour of the amorphous samples can be investigated by recording temperature-dependent Mössbauer spectra.

APPLICATION OF THE MÖSSBAUER SPECTROSCOPY FOR STUDIES OF IRON COORDINATION IN SILICATE GLASSES

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The possibly precise knowledge of iron ions valency and coordination in iron containing glasses is of importance for structural investigations as well as for the interpretation of their magnetic and electric properties. The Mössbauer spectroscopy has been used for investigation of the valence states and coordination numbers of iron cations in glasses. Measurements of ^{57}Fe Mössbauer effect were performed in selected potassium-alumino--silicate glasses. The influence of the preparation temperature of the studied glasses on the valence state and coordination number of iron cation is discussed. It was found that Fe^{3+} ions are present both in tetrahedral and octahedral coordination, while Fe^{2+} ions are only octahedral coordinated. In some, partly crystallized glasses both Fe^{3+} and Fe^{2+} cations were found to occupy only sites of tetrahedral coordination in glass matrix. The ^{57}Fe Mössbauer spectroscopy indicated the presence of a magnetic phase in some of glasses. The phase was identified as the magnetite. The devitrification process is marked by the magnetite-hematite transformation, along with the creation of new phase - mullite and the decrease of iron content in glass matrix. The Fe^{2+}/Fe^{3+} ratio derived from the Mössbauer experiments was confirmed with electrochemical techniques. The phase composition of samples subdued the crystallization was confirmed with X-ray diffractography and with electron microscopy.

PS 101

MÖSSBAUER STUDY ON DISPROPORTIONATION OF WUSTITE PHASE IN THE IRON CATALYST FOR AMMONIA SYNTHESIS

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The model iron catalyst for ammonia synthesis containing ~30 wt % of wustite $Fe_{1-x}O$ has been studied. The catalyst was prepared in industrial conditions. The molten mixture of iron oxides (Fe_3O_4 and $Fe_{1-x}O$) was cooled slowly. It was the reason that wustites of different stoichiometries were obtained in solidified sample. Next the catalyst was heated at various temperatures in nitrogen atmosphere and changes of the catalyst composition were followed by means of Mössbauer spectrometry. Mössbauer spectra were fitted using a model of two sextets for magnetite phase and of two doublets for two different wustite phases. The wustite of higher stoichiometry disappeared faster than the other one. A dependence of Mössbauer parameters of the phases present in the catalyst upon the temperature of heating is to be presented in some details.

POSTERS PS 63 - PS 75

Mass Spectrometry

PS 63

FAST ATOM BOMBARDMENT AND COLLISIONAL ACTIVATION MASS SPECTROMETRY OF OLIGOSACCHARIDES RELATED TO XYLANS

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Oligosaccharides related to D-xylans and D-glucurono-D-xylans were studied by using FAB, MIKE and CA mass spectrometry. FAB spectra of underivatized D-xylooligosaccharides offered reliable information on molecular weight. Esterification or partial etherification improve the useability of FAB spectra for determination of the mass of monosaccharide units. By employing FAB ionization and measuring MIKE and CA spectra of additive $[M+Glyc+H]^+$ ions, (1→2), (1→3) and (1→4)-linked D-xylobiose were studied. From the FAB CA spectra it is possible to estimate unequivocally the linkage type of dimers. The small values of discrepancy factors in the FAB CA measurements (0.03-0.06) prove that CA MS is also in combination with FAB ionization the most precise of the current mass spectrometric techniques.

DETERMINATION OF MEPAMIL METABOLITES BY MASS SPECTROMETRY

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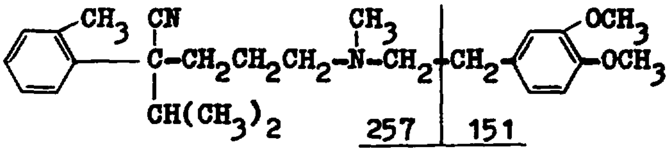
Mepamil is an original Czechoslovak calcium channel blocking agent. The structures of its metabolites were determined in rat, dog, and human urine by means of mass spectrometry after extraction and separation by TLC on silica gel.



Two of the metabolites originated by simple metabolic cleavage. Interpretation of their mass spectra led to the structure of N-demethylated metabolite (M = 394) and of N-demethylated product of α-amino cleavage (M = 244, base peak m/z 44). Interpretation of the spectra of all other metabolites required a complex approach to all available ionization techniques in combination with some additional methods, e.g. derivatization.

The very little abundant molecular ions of mepamil fragmented rapidly by β-amino cleavage under formation of base ions $(M-151)^+$. It was necessary to apply both EI and CI ionization methods to distinguish these fragment ions from molecular ions of the respective metabolites. Some of such metabolites, formed by α-amino metabolic cleavage, had considerably modified trimethylene chain. Exact mass measurements showed the presence of oxygen atom.

PS 65

QUANTIFICATION OF ISOSORBIDDINITRATE IN BLOOD PLASMA BY NEGATIVE ION CHEMICAL IONIZATION MASS SPECTROMETRY

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Negative Ion Chemical Ionization (NICI) Mass Spectrometry is a very effective method for quantification of drugs in biological materials thanks to its high selectivity. Electron Capture NICI with methane as a reagent gas produces intensive ions in the mass region of molecular ions ($[M]^-$; $[M-1]^-$; $[M+Cl]^-$), or fragment ions in the low mass region ($[F]^-$). For Selected Ion Monitoring is the first category generally preferred, because (i) the chemical noise is lower in the higher mass region, and (ii) deuterium labelled analogs can be employed as ideal internal standards.

Isosorbiddinitrate is an example of compound producing intensive fragment ions NO_3^- (m/z 62) and NO_2^- (m/z 46) under Electron Capture NICI. The fragments m/z 62 appear in NICI mass spectra only sporadically in contrast to m/z 46. We took advantage of this feature to work out methods of isosorbiddinitrate determination in blood plasma. As an internal standard was chosen isomeric isomannitdinitrate with identical fragmentation pattern.

Two procedures are described: a brief extraction with detection limit of 50 pg/ml plasma, and a more laborious one with detection limit of 10 pg/ml plasma. The results obtained with Selected Ion Monitoring were compared to Electron Capture Gas Chromatography which had similar detection limits but was about ten times slower.

LOW RESOLUTION GC/CIMS IDENTIFICATION OF 1,1,1-TRIMETHYLOLPROPANE ALLYL ETHERS AND THEIR ACETATES

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1,1,1-Trimethylolpropane allyl ethers (TMOP-AE) are among important components of some polyester resins and their evidence,differentiation or identification is often necessary. Electron impact (EI) ionization as well as methane and isobutane chemical ionization (CI) mass spectra were investigated of ten compounds having all possible combinations of hydroxyl, allyl and acetyl functional groups arising from TMOP-AE,present in a polyester sample, after the chemical cleveage of the polymer and derivatization reaction with acetic acid anhydride.

None of the EI spectra exhibited the molecular ion peak and to differentiate among individual compounds the spectra have to be inspected for differences in relative abundances of fragment ions.

The chemical ionization mass spectrometry, and especially that using more "soft" isobutane reaction gas, is most widely used for molecular weight determination only and it is often considered to be a technique which does not generally provide sufficient amount of information to allow for the differentiation among similar compounds or for their identification.
In our case, however,information about just only four characteristic ions (quasimolecular ion and three fragment ions representing elimination of water, acetic acid or allyl alcohol molecule) in the isobutane CI mass spectra permitted the simple scheme to be developed with the aid of which a rapid and easy identification of each particular compound among ten possible derivatives can be made without the need to compare the reference spectra.

PS 67

METHANE CIMS AS A TOOL FOR SELECTIVE DETECTION OF POLYESTER BIFUNCTIONAL CONSTITUENTS ON THE CHROMATOGRAM

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The bifunctional constituents of polyesters / dicarboxylic acids, diols / being converted into convenient gas chromatography derivatives produce characteristic methane chemical ionization (CH_4 CI) mass spectra that enable to detect these compounds on the chromatogram besides other interfering components.

CIMS is often used as a complementary method to electron impact mass spectrometry. The goal of analytical CIMS is to obtain a signal of quasimolecular ion and to determine the relative molecular mass of the compound in this way. However, with methane used as a reactant gas the specific elimination of small molecules from the quasimolecular ion occurs, and the adduct ions resulting from the reaction between methane plasma and analyzed molecule are present in the spectrum as well. These apparently excessive ions can serve for the relative molecular mass confirmation and, in addition, these ions state much about the functional group present in molecule.

The pattern of these spectra with particular classes of compounds are characteristic in such a degree that they can be used for the specific detection or even identification of bifunctional compounds / e.g. dicarboxylic acid dimethylesters, alkanediol-diacetates / on the chromatogram besides monofunctional compounds / e.g. modifying fatty acid methylesters / and also for distinguishing them from other present compoundsin the sample such are solvent residuals or blank components.

MASS SPECTRA OF ACRYLIC AND METHACRYLIC ACIDS ESTERS

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Most of the aliphatic alkyl and isoalkyl esters of acrylic and methacrylic acids are commonly used monomers. Because of the properties of the polymerized materials are influenced by the structure and quantity of the monomers there is a great need for suitable methods of their identification and determination.

This work is concerned with the possibilities of using mass spectra for the identification of acrylate and methacrylate monomers. The electron - impact /EI/ and chemical ionization /CI/ techniques were applied to the homologous series of 38 C_1 - C_{18} n-alkyl and C_3 - C_6 isoalkyl acrylates and methacrylates. With all esters a significance of the main fragment ions in the EI and in the both methane CI and isobutane CI mass spectra for the identification was studied. Simultaneously the major decomposition modes are shown and the effects of the isomerization as well as elongation in the alkyl chain were examined. The dependence of ion abundances on chain length with chemical ionization mass spectra of the series of methyl up to octadecyl esters are displayed.

PS 69

THE MASS SPECTROMETRY STUDY OF DIAMANTOID HYDROCARBONS DERIVATIVES

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In our laboratory, the mass spectra of diamantoid hydrocarbons derivatives have been investigated, for many years.

Most of mass spectra were taken on the single focussing magnetic type mass spectrometer LKB 9000. The mechanism of fragmentation those compounds have been found; it enables to determinate the type and the position of substituents.

At present, the parallel measurements are provided on the instrument ITD Finnigan MAT.

The spectra from both instruments are very similar in many cases and therefore, the conclusions about fragmentation mechanisms obtained on LKB 9000 are possible to applicate for ITD, too. However, in some cases, differences among spectra obtained on both spectrometers and differences among spectra from one chromatographic wave have been found.

The explanation of these effects will be discussed in this work.

FRAGMENTATION MECHANISM OF MODEL SUBSTANCES

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Deuterated standards and quantum chemical methods of various levels of approximation (MNDO and ab initio) were used for the interpretation of mass spectra. Acetone and acetaldehyde were chosen as model substances because of their structural similarity (R-CO-R) and relative simplicity that is important for theoretical treatment. Experimentally obtained spectral data were correlated with theoretical results of our calculations. Structural parameters, SCF-total energy, ionization energy and potentials, electronic structure, charge distribution, electronic density and bond order at various points of potential energy surface provide information about fragmentation mechanism. Experimental and theoretical results were in good agreement.

PS 7

MASS SPECTROMETRY OF STILBENES: E BROMOALKOXYSTILBENES

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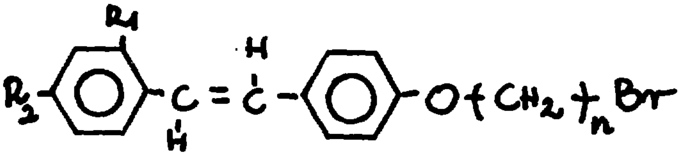
Substituent effect in the electron impact induced fragmentation of E stilbene has been the subject of different studies. We reported previously on the mass fragmentation of some derivatives of E stilbenol-4[1,2] and it heterocyclic analogs[3]. Our investigations have now been extended to fragmentation of 9 unknown in the literature E 4-bromoalkoxystilbenes of potential biological activity.



R_1=H,NO_2 R_2=H,NO_2,Cl,Br n=3,4,5,6

Based on metastable transitions and exact mass determinations the principal mass fragmentation of compounds 1-9 are proposed and discussed. It has been found that the basic mass fragmentation of investigated compounds is due to cleavages $C_{sp}3$-Br and $C_{sp}3$-O bonds of bromoalkoxy group. On the basis of the obtained data it has been established that the fragmentation patterns of E 2',4'-dinitro-4-bromoalkoxystilbenes include an oxygen transfer from the 2' nitro function onto $C_{sp}2$-$C_{sp}2$ moiety followed by several rearrangements. This may be viewed as a classical example of a complex ortho effect.

This work was supported within the project RP.II.13.

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MASS SPECTROMETRY OF THIO ANALOGS OFPYRIMIDINE BASES: E STILBENYLOXYALKYLTHIOURACILS

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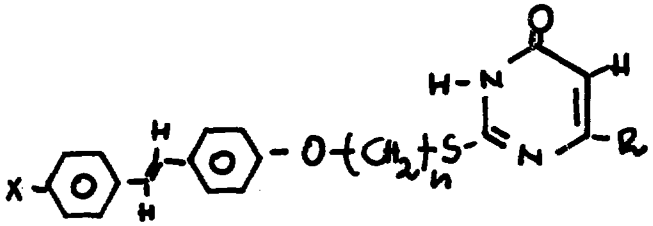
Mass spectra of uracil derivatives which are of great interest in connection with the biologically important nucleosides, nucleotides and nucleic acids have been examined in details. However, very little work has been published on mass spectra of thio derivatives of uracil. In continuation of our previous work on mass fragmentation of thio analogs of pyrimidine bases we present the fragmentation of 12 new E stilbenyloxyalkylthiouracils



x=Cl,Br n=3,5 R=H,CH_3,COOH

Based on metastable transitions and exact mass determination the principal mass spectral fragmentation routes of compounds 1-12 are discussed. The first steps in the mass spectral fragmentation of 1-12 are due to cleavage of the $S{-}C_{sp^3}$ and $O{-}C_{sp^3}$ bonds of the stilbenyloxyalkylthio group. The molecular ions of 1-12 do not undergo elimination of the •SH radicals, which are the specific fragmentation reactions of 2-alkylthio[1]- and 2-alkoxycarbonylalkylthiouracils[2].

This work was supported within the project RP.II.13.

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PS 73

INVESTIGATION OF CHEMISORBED LAYER ON METAL SURFACES BY THERMAL DESORPTION SPECTROSCOPY

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The chemisorbed layers on metal (especially tungsten and Ni-P alloy) have been investigated by thermal desorption spectroscopy - mass spectrometry.

This technique is based on heating the sample by a know temperature-program in a vacuum chamber and measuring the partial pressure during this procedure. The thermal desorption spectrum is the desorption rate - temperature curve, which can be calculated from the pressure-time curve.

The information obtainable from the spectra included the following parameters: the amount of the adsorbed gases, the activation energies and kinetic orders of the desorption processes - referring also to the adsorption mechanism.

The experimental equipment used in these studies was a desorption spectrometer connected with a quadrupole mass spectrometer, so that also quantitative analysis of the desorbed gases could be carried out.

AN UHV QUADRUPOLE GAS ANALYZER

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The analysis of the gas composition of vacuum tubes is important in their research and development and also for the routine quality check in the production. For example in our institute we have studied the gas contents in discharge tubes. That is why an UHV quadrupole gas analyzer with a tube breaking mechanism has been designed and constructed in our laboratory. The quadrupole mass spectrometer with mass range 1-300 u is placed in an UHV water cooled analytical chamber. The analytical chamber is connected with gas inlet system containing the mechanism of the tube breaking under vacuum. Usually the gas amount available in vacuum tubes is relatively small and therefore the pumping and inlet systems are designed also for very small gas flows (quasistatic mode of operation). The quadrupole gas analyzer is coupled with a 64 kbyte microcomputer.

PS 75

GC-MS ANALYSES OF LIQUID CRYSTALS

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Abstract not delivered

POSTERS PS 76 - PS 87
PS 95 - PS 96

Instrumental Radioanalytical Methods

PS 76

RNAA OF MULTIELEMENT REFERENCE MATERIALS BY THE k_0-STANDARDIZATION METHOD. COMPARISON WITH OTHER TECHNIQUES

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The growing need for multielement analysis on a large number of samples has compelled activation analysis to simplify its standardization procedures. With regard to this tendency, it seems that for general use the so-called absolute method is the most convenient. However, when using the absolute method, an arbitrarily selected nuclear data set must be used, usually introducing large uncertainties in the results. To overcome this difficulty, the k_0-standardization method was proposed by A. Simonits et al., which substitutes the arbitrarily selected nuclear data by composite nuclear constants (k_0-factors) experimentally determined with high accuracy.

The k_0-standardization method was implemented at LNETI, with two EG & ORTEC hyperpure germanium detectors: a coaxial and a gamma-X covered with a 1mm foil of copper. From the analysis of reference materials, we conclude that the k_0-method has an accuracy better than 10% for the experimental conditions used at LNETI (thermal neutron flux $\approx 10^{11}$ neutrons.cm^{-2}.s^{-1}; maximum continuous irradiation time available: 14h).

In this work, the k_0-standardization method is applied to reactor neutron activation analysis (RNAA) of the reference materials NBS SRM 1572 Citrus Leaves; NBS SRM 1573 Tomato Leaves; IAEA CRM SL-1; Jenoptik Jena GmbH Kalkstein KH; and marble MCG. At the INW (Gent), the latter is a candidate multielement standard for archaeology. The results are compared with published values obtained by different methods: relative method (RNAA), radiochemical NAA, epithermal NAA, and atomic absorption spectrometry. In the comparison, a good agreement is found.

SOME EXPERIENCES WITH INSTALLING THE k_0- METHOD OF NEUTRON ACTIVATION ANALYSIS AT THE INSTITUTE "JOŽEF STEFAN", LJUBLJANA, YUGOSLAVIA

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Abstract

The k_0-method of neutron activation analysis, developed at the Institute for nuclear sciences, Gent, Belgium and the Central Research Institute for physics, Budapest, Hungary, is being installed at the Institute "Jožef Stefan", Ljubljana, Yugoslavia. Neutron flux characteristics of the TRIGA MARK 2 reactor (thermal to epithermal flux ratio, deviation of the epithermal flux from the ideal distribution, flux stability) are measured by suitable flux monitors (^{197}Au, ^{94}Zr, ^{96}Zr, ^{64}Zn, ^{68}Zn, ^{98}Mo, ^{100}Mo, ^{112}Sn, ^{124}Sn, ^{54}Mn). HPGe detectors' reference efficiency curves are obtained for 50-3000 keV energy range by using calibrated point gamma-sources. Detectors are coupled to a VAX/VMS-750 computer, but also to the PC's. Relevant computer programs are implanted to perform rather complex calculations of the elements concentrations in a sample.

PS 78

A USER-ORIENTED TABULATION OF TRUE-COINCIDENCE CORRECTION FACTORS

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In absolute counting of sources close to a germanium detector, the effect of true-coincidence with cascading gamma or X-rays can lead to errors of several tens of percents in the evaluated peak areas. This is for instance the case in reactor neutron activation analysis (NAA) based on the k_0-standardization method [1].

Procedures for the calculation of true-coincidence correction factors have been described in literature, relying on the knowledge of the cascading structure in the decay scheme, on a number of nuclear decay constants, and on the experimentally measured detection efficiency[2, 3].

Whereas a rigourous correction leads to residual uncertainties better than ∿ 1.5% (even for close-in counting geometries), this is not required in some fields of application, where accuracies of the order of 5-10% are satisfactory. Therefore, in the present work a user-oriented tabulation is given of calculated true-coincidence correction factors for the most relevant gamma-lines of 138 radionuclides of interest in NAA. The data refer to measurements at 6 discrete distances to a 101 cm^3 Ge-detector (ranging from 17 cm to the top of the detector). The following effects are included : γ-γ coincidence summing and loss, γ-KX coincidence loss, identical gamma-rays emitted by both a mother and a daughter isotope, and delayed γ-γ emission.

The tabulated, exemplary correction factors reveal at a glance the importance and the magnitude of true-coincidence effects.

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* Research associate of the National Fund for Scientific Research

PS 79

NEW DEVELOPMENTS IN INSTRUMENTAL RADIONALYTICAL TECHNIQUES

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Improved instrumental neutron activation techniques have been developed at N.R.C. "Demokritos", in order to face special analytical requirements, like high sensitivity and low matrix interference for trace element analysis in a variety of geological, environmental and other samples and high accuracy for nuclear fuel enrichment and burn-up determination, nuclear reference material certification and other applications. Special emphasis has been given to short-lived nuclide determination by delayed neutron counting and gamma spectrometry using a flexible home-made nuclear analyzer with a double pneumatic transfer system (PTS). For higher sensitivity, higher counting statistics has been achieved by cyclic activation (CA) analysis and sample size enlargement capability using a new PTS with larger tube diameter. In addition, the background can be reduced by automatic capsule-sample separation before the measurement and by their automatic rejunction capability before reactivation. Observed background increase, due to contamination mainly from liquid samples, can be avoided by triple sample containment, realizable with the new PTS. Matrix interference in case of multielement gamma spectrometry can be reduced by intermediate sample storage (ISS) and subsequent matrix background substruction, before recycling. For higher accuracy, CA is again necessary for ultrahigh counting statistics, combined with neutron flux adjustment, through the flexible PTS tube terminal, and ISS, to avoid high counting rates and radiation levels. A programmable logic controller-microcomputer and pneumatic sample changer serve for automation of short-and long-lived nuclide analysis, respectively.

PS 80

ANALYSIS OF OPTOELECTRONIC MATERIALS

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Single Crystals - Turnov

The routine controll by radioanalytical methods: especially instrumental neutron activation analysis (INAA) and autoradiography (ARG) used in the high-purity techlogy for the production of optoelectronic materials is discused in this contribution.

INAA is suitable for the multielemental determination in concentration levels less than 10^{-10} g/g, ARG is ised for the determination of the surface distribution of optically active dopants on single crystals.

The concentrations of trace amounts of impurities in preforms of optoelectronic fibres can be followed by means of these methods. The same methods can be used during a purity checking of input raw materials for the production of YAG, BGO, YAP etc. and for the purity determination of a final single crystals.

INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF THE OLD PAINTINGS

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Institute for Research, Production and Application of
Radioisotopes - Prague

The instrumental neutron activation analysis (INAA) was used for analysis of several collection of samples from the old verified paintings. The application of INAA for the verification of old paintings from different periods, countries, regions and painters was the aim of this work. This method is based on the comparison of the concentrations of the pigments impurities.

The special method of sampling of a great number of very small samples from paintings, without any substantial damage, was worked out. The samples ware taken during restoration. The results obtained by INAA show certain differences of concentrations of the pigment impurities, especially the impurities of lead whites. A correlation between the concentration of pigment impurities and the period and region of the painting origin has been found.

PS 82

PURITY FOLLOWING OF NEW SEMICONDUCTOR MATERIALS

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Radioisotopes - Prague

The development and production of new semiconductor materials includes also mastering of their production under the conditions of very high purity. The knowledge of the - uselly very low - concentrations of dopants and impurities is great advantage for both producers and users.

Determination of contaminants in various materials, especially if they are present in low concentrations, is a rather difficult task. The instrumental neutron activation analysis (INAA), can be rated among the methods that can be used for the simultaneous qualitative and quantitative determinations of a great number of elements present in low concentrations.

The application of INAA, which is used in our Laboratory for service analysis, for determination of trace amounts of elements in some new semiconductor materials (galliumarsenide, Ge-As-Se chalcogenide glass, $Bi_2Se_{3-x}S_x$) is the aim of this contribution.

INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF GEOLOGICAL REFERENCE MATERIALS

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Neutron activation analysis (NAA) is frequently used for certification of element concentrations in reference materials, particularly at trace and ultratrace levels. Characteristics of NAA that make it valuable for this purpose are inherent precision and accuracy, very low determination limits for many elements, essentially blank-free nature, and multielemental capability, especially in the instrumental mode (INAA).

In this work, INAA was employed to determine up to 37 elements in geological reference materials of Aragonite AK, Diatomaceous Soil KB, Feldspar ZK, Glass Sand SPS (producer the Institute of Raw Materials, Kutná Hora,Czechoslovakia), Iron Ore ZD (USSR), and Apatite concentrates (USSR and Poland). The elements determined were Ag,Al,As,Ba,Ca,Cd,Ce,Co,Cr,Cs,Dy, Eu,Fe,Gd,Hf,K,La,Lu,Mn,Na,Nd,Ni,Rb,Sb,Sc,Sm,Sr,Ta,Tb,Tm,Th,Ti, U,V,W,Yb,Zn. Their determination was carried out using short-time (1-3 m) and long-time (5-10 h) irradiations in the thermal neutron flux of 5.10^{13}n $cm^{-2}s^{-1}$ and high resolution gamma-ray spectrometry with HPGe detectors after suitable decay times. The purpose of the work has been to contribute for establishing, updating or extending a number of certified element values. The accuracy and precision of results obtained has been compared with certified and other existing values.

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COULD THE LIMESTONES BE A PARENT MATERIAL FOR THE KARSTIC BAUXITES FORMATION ?

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Abstract

Genetic relation between the karstic bauxites and their carbonate footwall or the weathering crust is not obvious. Several theories exist about the formation of these bauxites, the theory of terra rossa being the most popular. According to this theory, the karstic bauxites are formed from the limestones. By studying the rare earth elements (REE) relative distribution patterns, we tried, in a way not practiced up to now, to elucidate this topic.

REE concentration in the limestones are rather low (from a hundredths ppm to a few ppm level) and are determined by means of instrumental neutron activation analysis. Samples are irradiated twice, for a short (5 minutes) and a long (7 hours) period. During 30 days after irradiations, their gamma spectra are measured for several times on a planar and a coaxial Ge(Li) detector. Computer programs, developed for this purpose, are used to analyse the spectra. We determined 12 of 14 naturally occuring REE; for 3 of them (Gd,Ho,Tm) the results obtained are not reliable enough. 6 samples of bauxites, 5 of limestones and 1 of terra rossa (all of them from the region of Montenegro, Yugoslavia) are analysed.

It turned out from studying the REE concentrations and their relative distribution diagrams, not to be likely that the limestones could give the source material for the bauxite formation. However, the definite conclusions can not be made before investigating the REE in the insoluble limestone residium. The REE distribution characteristics in the terra rossa sample are found to be quite similar to those ones in the bauxites. This asks for further studies.

DETERMINATION OF MICROGRAM AMOUNTS OF Am BY THE GAMMA-SPECTROMETRIC METHOD OF ISOTOPE DILUTION

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Small amounts of Am, both in spent fuel or Pu samples, are usually determined mass-spectroscopically /1,2/ or alpha-spectrometrically /3/, using the isotope dilution method, or by means of the measurement of total alpha activity /4,5/. Am-243 serves as a spiking isotope. For the method based on the measurement of total alpha activity, the isotope composition of Am has to be known and moreover Am must be qualitatively separated for the spent fuel samples. For both methods based on isotope dilution, Am ought to be isolated in pure form because the presence of isobares (Cm-242, Cm-243) or isotopes which emit the radiation of the same energy (Pu-238) interfere with the determination. The method of isotope dilution based on the evaluation of gamma radiation is free of the above disadvantages.

Americium $\leq$ 0.2 μg was isolated from a Pu sample on a column packed with anion exchange resin OSTION AG LT (200 - 400 mesh) in 9M HCl; after the isolation of Am from the spent fuel samples, the Am fraction contains the predominant part of fission products, which is separated in the further step - i.e. the separation on a similar column in a mixture of 90 % glacial acetic acid + 10 % 5M HNO_3. Am is eluated with 1M HNO_3. The Am-containing fraction is evaporated and the gamma-radiation emitted by Am-241 and Am-243 of 59.54 and 74.67 keV, under defined geometry, is measured. For the measurement, both a planar HPGe detector (area

1 000 mm^2, thickness 8 mm) and a high efficiency HP-Ge detector were used. The exposure was 1 000 s.

The Am-241/Am-243 isotope ratio is evaluated from the equation

$$\text{Am-241/Am-243} = \frac{A_1}{A_3} \cdot \frac{Y_3}{Y_1} \cdot \frac{T_1}{T_3} \cdot \frac{E_3}{E_1} \qquad (1)$$

where

A_1, A_3	are the intensities (areas) of the gamma radiation peaks emitted by Am-241 and Am-243, resp.
Y_1, Y_3	are the gamma radiation yields of the given energies of Am isotopes (6)
T_1, T_3	half-lifes of Am isotopes
E_1, E_3 ·	gamma-ray counting efficiency

By the similar method, Am is isolated, the gamma-ray counting is measured and the isotope ratio of the sample spiked with Am-243 is evaluated. The concentration of Am in the sample is calculated from the weighed amounts of the sample and the spiking isotope, further from the isotope ratio values determined during the measurements of Am enriched in spiking isotope, Am in the sample and in the mixture of spike with sample, by means of the relation used usually in MS IDA /2/.

By the method described, $\leq 0.2\,\mu$g Am can be determined with an error of ≤ 0.8 relative %; the results obtained agree well with those of the mass-spectrometric isotopic dilution method, the analysis costs as well as time consuption being decreased by ~ 50 %.

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PS 86

GAMMA-RAY SPECTROSCOPY USED FOR TRIBOLOGICAL DIAGNOSTICS

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Service life and reliability of machines depend substantialy on the wear of their constituent parts. Among the methods used for the study of wear, the radiotracer technique offer several advantages. In particular, it permitts evaluation of wear without dismantling the tested machine parts and it features very high sensitivity.

The method has been used for continuous wear study of diesel engine parts, such as cylinder liners, piston rings, elements of fuel injection pumps and valve lifters. Before the tests, the machine parts surface had been irradiated with cyclotrone accelerated charged particles. The wear was evaluated within the range of proportionality between the thickness of the worn-off layer and the measured gamma-ray activity of the wear debris.

If the wear of two different parts, made of the same material, is to be measured simultaneously, the respective friction surfaces are irradiated with two different kinds of particles which create different radioisotopes. The wear debris coming from the two individual parts can then be resolved by means of gamma-ray spectroscopy. In the field tests a high resolution semiconductor Ge(Li) detector was used in connection with a portable 1024 channel PH analyser.

Statistical methods were applied for the data evaluation in order to estimate the long term reliability of the machine under test.

AN ASSESSMENT OF THIN LAYER ACTIVATION AND GAMMA-RAY SPECTROSCOPY FOR TWO-COMPONENT MEASUREMENTS OF WEAR

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The thin layer activation by charged particles has been introduced for distinguishing the wear properties of two components /surfaces/ of the same iron based material.

For one component has been chosen activation with protons, for the other one activation with deuterons. Both types of activation create the ^{56}Co and ^{57}Co radionuclides ;their relative content and the specific activity distributions in the layer depend on the energy of the accelerated particles . The wear debris from both of them are estimated by monitoring the radioactive content of circulating medium using gamma-ray spectroscopy .

The optimum conditions for activation were derived from measurements of the gamma-ray activity in a stack of iron foils irradiated with a Ge/Li/ or a NaI/Tl/ detector . As can be deduced from these curves, activation with 14,5 MeV protons and 8,3 MeV deuterons is suitable.

To facilitate calculations of individual activities and their interferences, an aproximate method for quantitative evaluation of gamma-ray spectra has been worked out.

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DISTRIBUTION OF THE NATURAL RADIOISOTOPES IN THE SEDIMENT SAMPLES FROM NORTH-BOHEMIA COAL BASIN

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The contribution states some results of the geochemical study of the Tertiary sediments from North-Bohemia brown-coal basin.

The main interest was to determine the distribution of natural radioisotopes (U, Th and K) evaluating gammaspectrometry results of drill-core samples from the region studied.

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FAST SPECTROMETRY OF NATURAL ENVIRONMENT RADIOACTIVITY FIELDS

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Abstract not delivered

POSTERS PS 97 - PS 99

Electron and Ion Spectrometry

PS 97

THE AUGER N(E) SPECTRUM MEASUREMENT USING BBM METHOD

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In Auger electron spectroscopy there are three different methods which can be used to measure the N(E) spectrum:

- The direct measurement of detector output signal when the modulating voltage is not applied to the CMA,
- the pulse counting technique,
- the beam brightnees modulation (BBM) technique.

The last mentioned method has several advantages.

1. It is possible to applicate it in the Auger spectrometers with classical method of d N(E) / dE spectrum acquisition. The modification of the Auger spectrometer involves the additional primary electron beam modulator. The signal detecting and processing electronics is not changed.
2. BBM method in comparing to classical spectrum measurement method gives better signal-to-noise ratio. This fact permits the electron beam intensity reduction. In consequence of this reduction the radiation damage should not be significant.
3. BBM method can be used over a wide range of electron beam intensities (10^{-5} to 10^{-11} A).

The Auger spectrometer which is able to work in classical mode of spectrum acquisition as well as in BBM mode is described. This spectrometer is ON-LINE connected to the microcomputer SM 50/50. In the main part of contribution the comparision of two analytical methods - the classical and BBM is presented from the viewpoint of the sensitivity and the accuracy in quantitative analysis.

THE INFORMATION DEPTH OF DIFFERENT KINDS OF THE APPEARANCE POTENTIAL SPECTROSCOPY

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A model of transport processes influencing the intensity of the signal in the Appearance Potential Spectroscopy (APS) has been proposed in |1|, |2| and developed for layered structures for the Disappearance Potential Spectroscopy (DAPS) and Soft X--ray APS in |3|, |4|. It is based on the description of possible elastic and inelastic interactions of electrons with individual atomic layers in the solid. Mean probabilities of these interactions are introduced, the processes are supposed to be isotropic. In the present paper the model is applied also to the Auger Electron APS (AEAPS), where slowing down of the Auger electrons and formation of tertiary electrons by a cascade process is supposed. The information depth-defined as the thickness of surface layer from which 90% of the signal arises - is calculated for different parameters involved. The results are compared with the existing experimental data.

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PS 99

AB INITIO THEORY OF THE SPECTRA OF THE IMPURITY CRYSTALS

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Calculation of the spectral properties of impurity crystals is very complex problem of solid state physic. The last years the X_α- method by J.Slater developed very intensity for different compounds. For crystals doped by 3d- and 4f-ions this method is difficult and for this systems we proposed the new method - method of the self-consistent field for impurity crystals /1-2/. If we consider the spectral properties of a crystal doped by ions with nl^N-configuration ($nl=3d,4f$, etc.) an impurity ion and surrounding ones can be chosen as a cluster. The wave functions of the ions in a cluster are easily obtained as solution of the Hartree-Fock modification equations:

$$\left[\frac{d^2}{dr^2} + \frac{2}{r}Y'(nl|r) - \varepsilon_{nl,nl} - \frac{l(l+1)}{r^2}\right]P(nl|r) = X'(nl|r) + \sum_{n\ni n'} \varepsilon_{nl,n'l}P(n'l|r)$$

where Coulomb potential $Y'(nl|r)$ and exchange one $X'(nl|r)$ differ to corresponding Hartree-Fock potentials by terms $\Delta Y(nl|r)$ and $\Delta X(nl|r)$ /2-3/. The additional terms depend on the electronic state of impurity ion, surrounding ones and intraionic distance. The equations for impurity cluster must be solved with corresponding boundary conditions /2/.

Analysis of the solutions of our equations for 3d- and 4f-ions in different crystals allows to come to conclusion about full qualitative and well quantitative agreement empirical data for optical, magnetic and other properties of the impurity crystals. The best results we have received for pressure dependence of spectra of Cr^{3+} ions in ruby, Nd^{3+} in YAG /1-2/, optical and X-ray spectra and chemical shifts for Cr^{4+} and Cr^{2+} and other ions in various crystals /3-4/.

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POSTERS PS 26
PS 42 - PS 45
PS 88 - PS 94

Environmental Analysis

PS 26

CORROSION OF ST. VITUS CATHEDRAL MEDIEVAL MOSAIC BY POLLUTED ENVIRONMENT

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The blue, red, green, yellow and other more than 28 varieties of coloured tesserae of glass created beautiful mosaic of The Judgement Day on the exterior wall of the St. Vitus cathedral. More than 600 years the work of the Czech glassmakers ordered by the Emperor Charles IV. has been wethered and due to the atmospheric attack, its corroded nontransparent surface layer burries the structure of original mosaic picture. Three previous restorations tried to conserve the mosaic as the whole, however, they failed to stop the ion exchange process, which is assumed to trigger the corrosion of the medieval glasses in aqueous solutions. Almost all these glasses are characterized by an unusually high content of potassium and calcium. According the previous studies, leached components react with the ambient atmosphere (CO_2, NO_x and mostly with SO_2) and the main component of weathering products are gypsum and syngenite.

Blue glass samples with approx. 47 % SiO_2, 28 % CaO and 25 % K_2O have been studied by XPS, SIMS, SEM, EPIMA and X-ray diffraction to obtain surface analysis of the morphological and chemical changes which take place during the weathering. Analysis of the particular tesserae has shown in addition to the presence of the usual corrosion products new aspects: The topmost layer is formed mostly by SiO_2, the glass under the corrosion layer is leaked and cracked. Number of glassy spheres originating from coal heating outlet was found on the surface.

DETERMINATION OF HEAVY METALS IN FOOD PRODUCTS

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In the Technical University of Lublin there have been conducted for many years studies on the use of spectrometric fluorescence to determine trace elements in food products both of vegetable and animal origin.

The research was conducted with the use of fluorescent X-ray spectrometer of VRA-2 type of Carl-Zeiss Jena.

The trace elements (vanadium and wolfram) were being determined in food products: beef kidney and beef liver. In the case of products it was necessary to carry out thermic mineralization at the temperature of 550°C. The angle of inclination of an analising crystal during spectrometric measurements was as follows:

for V - 76,82°, for W - 42,99°.

The results of determinations have been shown in the table.

The studied food product	The contents of elements, mg/kg	
	V	W
Beef kidney	0,004	0,033
Beef liver	0,046	0,009

PS 43

ENERGY DISPERSIVE X-RAY FLUORESCENCE ANALYSIS OF FALL-OUT OF DUST

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A procedure for analysis of fall-out of dust and atmospheric precipitation by energy dispersive X-ray fluorescence with radioisotopic excitation is described. The samples of limited amount were treated by drying, grinding and pelleting. The corrections for matrix effects were made. For standardization a standard reference material of trace elements in coal fly ash was used. The analyses were performed using the spectrometer consisting of semiconductor detector, radioisotopic source ^{109}Cd and multichannel analyzer NTA 1024 with programmable calculator EMG 666.

DETERMINATION OF SULPHUR ON WHATMAN FILTERS BY THE METHOD OF WAVELENGTH-DISPERSIVE X-RAY FLUORESCENCE

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In order to evaluate the long range transmission of air pollutants, in Czechoslovakia the Hydrometeorological Institute carries out measurements of SO_2 and SO_4^{2-} concentrations in the atmosphere by means of several stations. For sampling two Whatman filters arranged one after the other are used, the former collects aerosols and the latter, preimpregnated with KOH, collects SO_2. The SO_4^{2-} concentration has been determined up to now colorimetrically after leaching the filters with water on the basis of colouring the complex of Ba ions with Thorine.

On the basis of both the recommendation and the working manual of the EMEP and with regard to the working procedure of the measuring centre in the FRG, an X-ray fluorescence method of sulphur determination on filters has been validated in the Fuel Research Institute. In the application of this method the S contents are determined in the range 4 - 300 μg S on aerosol and KOH impregnated filters. The measurements are carried out by using a SRS-1 Siemens sequential X-ray spectrometer. To excite radiation, an X-ray tube with Cr-anode is used, after passing through the collimator of 0.42 mm the fluorescence radiation is dispersed with the PET crystal (2d = 0.875 nm) and the S K_α line intensity is measured by means of a flow proportional detector with inlet window of 2 μm thickness. Ring filters of 35 mm diameter are put in adapted sample holders, the diameter of the irradiated surface is 23 mm. During measurements the sample holders rotate, the measurement time of each side is 40 s.

For evaluation the sum of impulses measured on the two sides of the filter is used and corrected with reading off the sum of blank sample impulses measured on both sides.

The XRF intensities of actual filters are compared with those of standard Whatman filters, impregnated with a known amount of sulphates in aqueous solution. With respect to the different S-distribution profile within the actual field sample and within the filter standard and with respect to the X-ray radiation absorbed by a filter matrix, the contents obtained should be multiplied by the experimental factor 0.68. The resulting sulphur content related to the filter efficient surface is divided by the amount of air in the collecting equipment and expressed in $\mu g/m^3$ of air.

Under the given conditions of measurements the following metrological characteristics were obtained:

- Detection limit $D_l = 0.24\ \mu g$ S/f
- Sensitivity $S = 952$ imp/µg S
- Determination limit $D_L = 0.8\ \mu g$ S/f
- Precision better than 1.4 % rel. standard deviation
- Reproducibility better than 10 %

The accuracy was not evaluated due to the lack of suitable reference materials.

DETERMINATION OF Ca AND Sr IN BONES BY XRF ANALYSIS

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There is an assumption that the concentration of Sr in human bones depends on the composition of the meal. The higher concentrations of Sr may be expected in the bones of persons consuming namely vegatable meals.

The radionuclide XRF analysis was used for the determination of Ca and Sr in human bones dating from the 6 th to 7 th century. The ^{109}Cd radionuclide excitation source was used for excitation of characteristic X-ray of Ca and Sr in the bones. The semiconductor Si(Li) detector was used for X-ray measurement and the multichannel analyser has been used for registration of X-ray spectras.

The area ratio of K_{α} Sr line to K_{α} Ca line (K) was chosen as a measure of concentration level of Sr in the bones. We have observed the great differences in K factor for the horse bones and for human ones. The precission of the determination of factor K was also tested. The results of XRF analysis for Sr and Ca determination were compared with the archeological observations.

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DETERMINATION OF ASH YIELD IN COAL BY NATURAL GAMMA-RAY SPECTROMETRY

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Natural gamma-rays from the Silesian hard coal samples were measured by a scintillation spectrometer, applying a 3"by 3" NaJ(Tl) crystal and proper shielding. Three gamma-ray energy lines were used : 1.46, 1.76 and 2.63 MeV, for the determination of ^{40}K, ^{214}Bi (^{238}U) and ^{208}Tl (^{232}Th), respectively; there is assumed, that the radioactive equilibrium is preserved in such samples. The ash yield A (in wt per cent) was calculated from the following regression equation :

$$A = 4.66 + 0.068\ N_K + 0.21\ N_U + 0.20\ N_{Th}\ ,$$

where N_K, N_U and N_{Th} are concentrations of potassium in per cent, and of uranium and thorium in ppm.

For more than 50 coal samples of about 0.6 kg each, with the ash yield determined by other methods within the range of 2.8 to 63.6 wt %, the correlation coefficient was equal to 0.957 and the arithmetic mean of 95% confidence interval estimates $< \Delta_{95\%} >$ equal to 1.83 wt %.

The same N numbers can be used for a rough estimation of calorific value of coal Q (kJ/kg). In this case the correlation equation was found to be as follows :

$$Q = 30060 - 8\ N_K - 77\ N_U - 235\ N_{Th}$$

For the mentioned above set of samples the correlation coefficient was equal to 0.85 and $< \Delta_{95\%} > = 1580$ kJ/kg.

The method seems to be simple enough for the control of hard coal quality, mainly of its ash content. Accuracy of the determinations depends on the correlation between measured values and coal properties for a given coal field.

SELECTED PROCEDURES FOR EVALUATION OF SMALL RADIOANALYTIC DATA SETS

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The urge for the accuracy and efectivity increase of result evaluation obtained from radioanalytic methods leads to the intensive elaborating of procedures for exploitation of limited information, which is held in so called small data sets.

The contribution discusses selected procedures for evaluation of small data sets, used in geochemical research works.

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QUALITY ASSURANCE IN NEUTRON ACTIVATION ANALYSIS OF ENVIRONMENTAL SAMPLES

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Analytical data are used in many decision processes and their reliability has become a very important factor. To ensure a good quality and reliability of the data produced in neutron activation analysis (NAA) laboratory a systematic approach to a quality assurance (QA) should be used. The QA system developed for our NAA laboratory is based on the use of concurrent analysis of replicate samples of matrix-based certified reference materials (CRMs) with every sample batch. This approach similar to that one used in Los Alamos National Laboratory /1/ assesses both precision and accuracy of the results. The control charts based on the CRMs results are used to determine if our analytical system is in a state of statistical control and to visualize and monitor a long-term stability of the quality of the data produced.
The QA system works with a Digital Equipment Corporation PDP 11/34A computer system and gamma-ray spectrometers ND66 and ND65 produced by Nuclear Data. In-house software and databases have been structured around the PDP DATATRIEVE-11 software system and the Nuclear Data gamma-ray spectrometry and NAA software. The key program in the QA software is the program QA CHECK. The database of elemental concentrations in various CRMs has been formed from the certified values or from "concensus" values in the case of elements that are not agency-certified. The QA program is routinely applied to the INAA of aerosol, fly ash and coal samples. The CRMs produced by NBS (USA), BCR (Commission of the European Communities) and Institute of Radioecology and Applied Nuclear Techniques (Czechoslovakia) have been used. Other features of QA as intercomparisons etc. have been also employed.

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STUDY OF LEACHING CONDITIONS OF SOME HEAVY METALS IN SOILS BY AAS AND INAA

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Element transfert from contamined soils into groundwater, plants and foot-chain depends strongly on the leachability of particular element.

In this work, consecutive leaching of the elements As, Cd, Co, Cu, Fe, Mn, Ni, Pb, Sb and Zn from industrially contamined soils was examined by

1) neutral magnesium chloride solution (exchangeable metals)
2) sodium acetate solution at pH 5 (carbonate-bounded metals)
3) hydroxylamine hydrochloride solution in acetic acid (metals bound in seskvioxides)
4) nitric acid and hydrogen peroxide solution (organically-bound metals)
5) hydrofluoric and perchloric acid solution (silicate-matrix-bound elements)

To simulate acid rain effect leaching with dilute nitric and sulfuric acid solution (pH 2-4) was also studied.

The total content of elements in soils was determined by instrumental neutron activation analysis (INAA) while leachable portions of elements in solution were determined by atomic absorption spectrometry (AAS).

For INAA soil samples were irradiated at VVR-S reactor for 1-3 min and 10 hrs. The thermal neutron flux was $5.10^{13} n\ cm^{-2} s^{-1}$. Gamma-ray spectra were measured by high resolution and high efficiency HPGe coaxial detectors coupled to gamma-spectrometer system Nuclear Data 683. AAS measurements were carried out with Varian AA 875 ABQ spectrometer using calibration solutions in leaching media.

Accuracy of results was tested by analyses of IAEA Standard Reference Materials SOIL-5 and SOIL-7.

Correlations between leachable metals were also evaluated.

DETERMINATION OF ALKALI METALS AND RADIOCAESIUM IN MUSHROOMS

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Mushrooms are known to manifest an increased ability to accumulate some trace elements and radiocaesium as compared with vascular plants. Rb and Cs in mushrooms and in soils were determined by neutron activation analysis. The RdCs was determined by the gamma ray spectrometry. The differences between concentration factors of non radioactive Cs and RdCs from the radioactive fallout were orders of magnitude. No significant differences between concentration factors of the stable Rb and Cs were found for mushrooms and vascular plants. According to the known $^{137}Cs/^{134}Cs$ activity ratio in mushrooms and in soils it was possible to distinguish ^{137}Cs accumulated from the old nuclear weapon fallout and from the fresh 1986 fallout. The measured content of radiocaesium was used to calculate the dose of ionisation radiation caused by ingestion of edible mushrooms

INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF RARE-EARTH AND OTHER TRACE ELEMENTS IN SOILS.

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The knowledge of abundance and distribution of rare-earth elements (REE) in the environment has shown to be very helpful in geochemical and biological investigations (1-4).Moreover REE are used as indicators of the behaviour of transuranic elements in the environment on account of the similarity in their physico-chemical properties (5-6).Great effort has been devoted to the development of reliable analytical tecniques capable of providing accurate data on REE concentrations in terrestrial materials.Neutron activation analysis is,at the moment,the most used technique for the determination of REE on account of its high sensitivity and of the high quality precision and accuracy (7-9).
In the present paper a number of REE (La,Ce,Nd,Sm,Eu,Tb,Yb,Lu) and some other useful trace elements (Zr,Hf,Fe,Co,Sc,Th,U) were determined in an alluvial soil by instrumental neutron activation analysis.The soil samples were collected in an unpolluted area of the Po river valley (Northern Italy).The investigated elements were determined in successive layers, 5 cm thick,up to a depth of 50 cm.Soil samples, after being dried and homogenized, were irradiated in the TRIGA MARK II reactor of the University of Pavia at a thermal neutron flux of about $1x10^{12}$ n cm^{-2} s^{-1} .Induced radioactivity was measured by gamma spectrometry.The obtained data,together with their precision and accuracy,are given and discussed.The depth profile is reported as well.The data are correlated with some typical soil parameters, such as pH, granulometry, total organic carbon.Correlation between REE and the other determined trace elements are also investigated and reported.

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ELEMENTAL CHARACTERIZATION OF THE IAEA INTERCOMPARISON SAMPLES OF MILK POWDER BY NEUTRON ACTIVATION ANALYSIS

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The accurate determination of biologically important elements at trace and ultratrace levels in biological materials is associated with severe analytical difficulties. These problems were illustrated in a round-robin intercomparison of the IAEA Milk Powder A-11. The reported values for a number of elements varied over several orders of magnitude and a follow-up study was necessary to elucidate their levels.

New intercomparison samples of the IAEA Milk Powder-153 were analyzed along with already existing reference material IAEA Milk Powder A-11 as a control. Irradiations were carried out in a VVR-S reactor with the thermal neutron flux of 5.10^{13} n cm^{-2} s^{-1}. Radionuclide activities were counted with high resolution and high efficiency HPGe detectors coupled to Nuclear Data 683 gamma-spectrometer. The elements Br,Cl,Ca,Co, Cs,Fe,K,Na,Rb,Zn were determined by INAA while for the determination of Cu,Hg,I,Mn,Mo,and Se radiochemical procedures were necessary. Very good agreement was found between our results and the IAEA certified and/or literature values for element levels ranging from a few ng g^{-1} of Hg up to a few per cent of Ca in the Milk Powder A-11. This supports the validity of our results obtained for the IAEA-153 Intercomparison Study on the determination of inorganic constituents in milk powder.

LECTURES OF INSTRUMENT MANUFACTURERS

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NEW AND IMPROVED METHODS AND INSTRUMENTATION FOR SURFACE ANALYSIS WITH ELECTRON SPECTROSCOPY

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Surface Analysis with XPS, UPS, AES, ISS, SIMS and LEED is well accepted and widely applied in thin film analysis. Improvements in respect to quantitation, sensitivity and spatial resolution have been made during the last few years. New techniques like SPA-LEED and ELS give additional information on surface structure (LEED) and chemical composition of adsorbates on a surface (ELS)

This paper reports on recent developments in the field of:

- SSXPS	Small Spot XPS, with improved spatial resolution for small area analysis.
- SPA-LEED	Spot Profile Analysis Low Energy Electron Diffraction - a method to investigate the topography of solids.
- ELS	Electron Loss Spectroscopy with high energy resolution - a technique to get information of topological structure of innermolecular or molecule-substrate bond by studying of surface vibrations.

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ADVANCE IN HIGH RESOLUTION, HIGH COUNT RATE GAMMA SPECTROMETRY WITH TIME INVARIANT FILTERS

R. Soavi - SILENA S.p.A. - Via Firenze, 3 - 20063 CERNUSCO S/N

A new pile-up rejector circuit approach, that fits in conventional time invariant spectroscopy amplifiers is described.
The circuit includes a high-gain Fast Channel and two levels of pile-up inspection; at the first level the pile-up on the main channel is inspected, at the second a shape discriminator detects a pile-up occurring in the fast channel. The result is an enhanced peak to background ratio and remarkable reduction of sum peak area when operating at maximum throughtput rate.

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RECENT DEVELOPMENTS IN PERFORMANCE AND CONSTRUCTION OF ULTRA-LIGHT ELEMENT EDS DETECTORS

N.Wilkinson

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Since their first introduction for use on scanning electron microscopes, the use of windowless/ultra thin window detectors has become more commonplace. They offer the facility for very rapid qualitative analysis of the ultra-light elements and in some cases, fully quantitative analysis.

Recent advances in detector fabrication, coupled with advances in pulse processor electronics, have extended the useful range of these spectrometers to the detection of boron and in some cases, beryllium. This has resulted in better detection for the remaining ultra-light elements, carbon, oxygen, nitrogen etc.

The experience gained form extensive use on S.E.M.'s has led to the development of a new range of detectors for use on transmission and ultra-high vacuum microscopes. These detectors make extensive use of electronic and mechanical interlocking and automation for protection and ease of use.

The industry standard measurement of resolution using Fe55 now proves inadequate for performance testing in the ultra-light element range. A new test "peak to valley" is proposed for this purpose from Link Malcom Reynolds and Neil Wilkinson.

THE MS/MS CAPABILITIES OF A NEW ANALYSER SYSTEM

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A double focusing mass spectrometer has been previously described (1) which incorporates an air-cored electromagnet as the mass analyser. This yields advantages in both speed and controllability. In particular a very simple relationship relates the current passing through the electromagnet to the mass focussed.

$$M = kI^2, \quad \text{where } k = \text{constant} \qquad I = \text{coil current}$$

Extensive calibration procedures required when MS/MS experiments are performed on conventional sector hardware are removed due to the predicability of the mass on this novel instrument. MS/MS experiments can be demanded at any time without prior set-up. All three types of MS/MS experiment commonly used can be carried out in this manner (daughter scans, parent scans and constant neutral loss scans).

A brief description of the theory of the system's automated operation will be given together with some relevant applications.

(1) R.H. Bateman, P. Burns, R. Owen, and V.C. Parr, presented at the 10th International Mass Spectrometry Conference, Swansea, Wales, 1985.

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QUANTITATIVE BULK ANALYSIS AND DEPTH PROFILING OF HARD MATERIALS AND COATINGS WITH SNMS.

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The quantification of all elements in sputter equilibrium is possible with SNMS (Sputtered Neutral Mass Spectroscopy) since the postionization process is decoupled from surface sputtering. Therefore the relative elemental sensitivity is independent of the chemical composition of the investigated material (no matrix effects!). High erosion rates of 0,1 - 2 nm/sec by Argon ion bombardment from an RF-Plasma discharge can be achieved.

Thermal diffusion of mobile elements into the surface region during sputtering can be avoided by sample cooling with liquid Nitrogen.

A superalloy for turbines was analyzed. The accuracy of the composition was better than 2% for the main elements and better than 15% for trace elements in the range of 1 to 10 ppma. The depth profile analysis of a 6 um multicoated W / Co -alloy shows the capabilities of SNMS in the field of thin film analysis and material research.

SOME FAST ATOM BOMBARDMENT APPLICATIONS ON NOVEL MAGNETIC SECTOR MASS SPECTROMETER.

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The development of a mass spectrometer based on an electromagnet with a non-ferrous core has been described (Ref. 1). The magnet design leads to a number of advantages over conventional ion-cored magnets, including much improved ultimate scanning and switching speeds, and greater controllability of the magnetic field. The latter removes the need for calibration of the mass scale for nominal mass determination, and allows accurate mass measurements to be obtained simply and routinely.

These features are particularly useful in combination with soft ionisation techniques such as FAB and Thermospray, for which mass scale calibration is notoriously difficult.

A dynamic FAB has been developed in which sample is continually transported to the probe tip through a piece of tubing from outside the vacuum system. This has the advantage that only low concentrations of FAB matrix are required, which significantly reduces background interference and this improves detection sensitivity.

A cesium ion gun has been designed, which allows 10kV cesium ions to be used to ionise the sample. The reduced gas load of such an ion gun leads to improved sensitivity for high molecular weight compounds.

Results will be presented which demonstrate each of these techniques.

1) R.H. Bateman, P. Burns, R. Owen, V.C. Parr
in:- Advances - mass spectrometry, 1985, John Wiley & Sons P.863.

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IMPORT AND EXPORT OF STANDARD REFERENCE MATERIALS AND OTHER MATERIALS AND DEVICES FOR SPECTROSCOPY

Služba výzkumu, Prague, Czechoslovakia

Abstract not delivered

AUTHOR INDEX

VARRO

SILENA MULTICHANNEL ANALYZER

"Varro", the latest addition to SILENA's family of multichannel analyzers, represents an important advancement in MCA design and technology.

Like "CATO", "CICERO" and "LIVIUS", "VARRO" is designed to provide a high level of accuracy and stability in nuclear measurements, sophisticated data processing, combined with operator convenience and ease of use.

With its powerful 16-bit microprocessor, the "VARRO" MCA provides fast, high-resolution PHA and MCS data acquisition, flexible input/output facilities (the Floppy Disk is directly integrated into the analyzer Basic Unit), complete data display capabilities to meet a wide variety of different applications in gamma and alpha spectroscopy.

"VARRO" is surprisingly simple to operate. Its extensive, interactive menu is a built-in operator's manual allowing the first-time user to achieve immediate control of the MCA functions without the need for time-consuming consultation.

VARRO's enclosure is simple and attractive and provides space to accomodate and feed up to 3 NIM-standard modules (Pulse Amplifier, High Voltage Power Supply and Analog-to-Digital Converter).

The Floppy Disk Driver is built into the VARRO mainframe and can be accessed from the front-panel of the analyzer.

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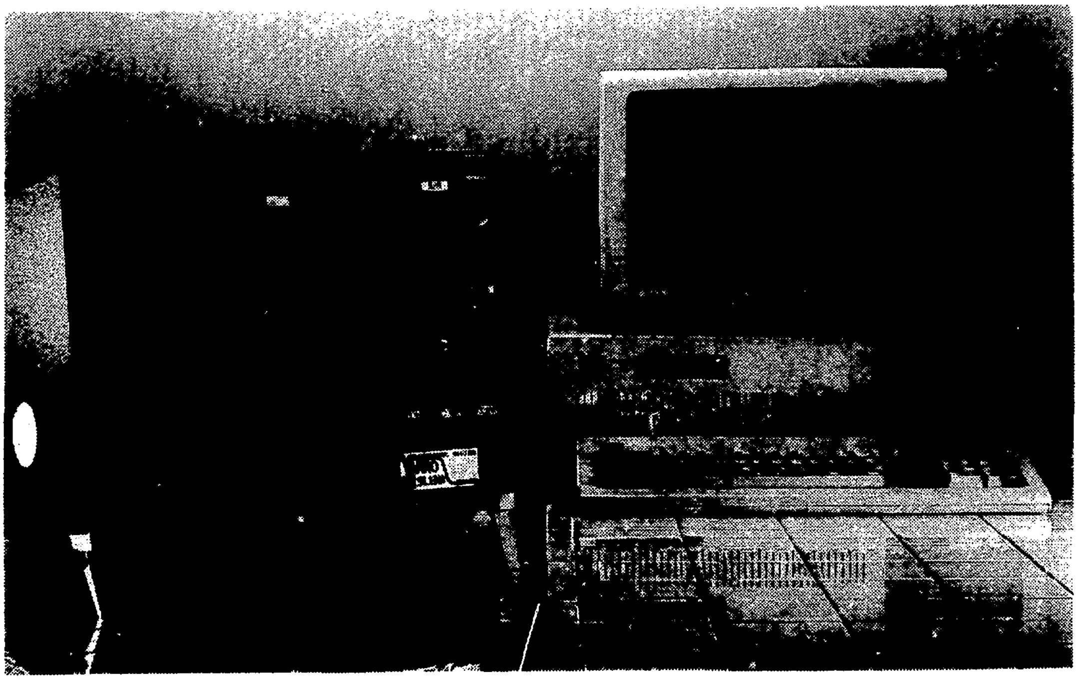

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