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ЛАБОРАТОРИЯ  
ДИАГНОСТИКА МАТЕРИАЛОВ

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СЕНТЯБРЬ

# ЗАВОДСКАЯ ЛАБОРАТОРИЯ

## ДИАГНОСТИКА МАТЕРИАЛОВ

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ЕЖЕМЕСЯЧНЫЙ НАУЧНО-ТЕХНИЧЕСКИЙ ЖУРНАЛ ПО АНАЛИТИЧЕСКОЙ ХИМИИ, ФИЗИЧЕСКИМ, МАТЕМАТИЧЕСКИМ И МЕХАНИЧЕСКИМ МЕТОДАМ ИССЛЕДОВАНИЯ, А ТАКЖЕ СЕРТИФИКАЦИИ МАТЕРИАЛОВ

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## ABSTRACTS

UDC 543.51

**The Use of Tandem Mass Spectrometry of High-Resolution with Data-Dependent Acquisition for Verification of the Authenticity of Peptide and Protein Drugs**

*Berizovskaya E. I., Vasiliev K. Y., Maksimov V. A., Ichalaynen A. A., Antochin A. M., Taranchenko V. F., Goncharov V. M., Mitrofanov D. A., Udintsev A. V., Aksenov A. V., Rodin I. A., Shpigun O. A.*

The use of high-resolution mass spectrometry in data dependent acquisition mode is presented for assessing the authenticity of peptide and protein based drugs. The parameters of mass spectrometric detection (e.g., capillary potential and temperature, range of the detected ions, ion population, maximum ion injection time for MS/MS, ranges of the ion charge state and mass variation, duration of dynamic exclusion, impact energy, isolation width) are specified.

**Keywords:** human recombinant insulin; human somatotropic recombinant hormone; high performance liquid chromatography; mass spectrometry; data dependent acquisition mode.

UDC 543.421:546.19

**Permanent Sorbent-Modifiers for Electrothermal Atomic Absorption Determination of Arsenic with Photochemical Vapor Generation**

*Burylin M. Yu., Romanovskii K. A., Knyaginichev A. V.*

The properties of permanent sorbent-modifiers (iridium, zirconium and tungsten carbides) are investigated with regard to trapping gaseous trimethylarsine and subsequent electrothermal atomic absorption determination of arsenic. Trimethylarsine is produced by photochemical vapor generation using an original reactor. Introduction of the activated carbon upon graphite furnace treatment with tungsten appeared expedience for production of carbide nanoparticles which enhance sorption efficiency. The parameters of photochemical vapor generation of trimethylarsine and thermal conditions of its trapping and atomization are optimized. The developed analytical scheme is applied for As determination in tap water. The absolute and concentration limits of As detection (calculated by 3s-criterion) are 0.38 ng and 31 ng/liter, respectively.

**Keywords:** electrothermal atomic absorption spectrometry; trapping; permanent modifiers; photochemical vapor generation; arsenic.

UDC 543.621:543.51:543.056:543.442.2:543.427.4:543.423.1:543.427.4

**Determination of the Occurrence Form of the Elements in Slags and Slimes of Vanadium Production**

*Zhdanov P. A., Seregina I. F., Bol'shov M. A., Volkov A. I., Seregin A. N.*

Complex study of the samples of technogenic raw materials (TRM) is carried out. Chemical and phase composition of the burned slag and slimes of vanadium production is performed using x-ray fluorescence spectroscopy and x-ray diffraction analysis. Sequential extraction of the chemical compounds of basic elements is studied according to the three-stage scheme recommended by the European commission is carried out. Low mobility of the aforementioned chemical compounds is observed. Compounds of vanadium and manganese in slag possess higher mobility compared to slime. Methods of atomic emission with microwave plasma (MP-AES) and mass-spectrometry with inductively coupled plasma (ICP-MS) are used to determine the total content of V, Mn, Fe, Cr, Zn, Ni, Ba, Sr, Rb, Y, Ga, Ge, Mo, La and Ce in slag and slime samples. Iron and chrome form strong oxides with silicates which can be digested only by HNO<sub>3</sub>. It is found that the total concentrations of V, Mn, Cr in those waste materials significantly exceed the upper limit of permitted concentrations of these elements in soils. A possibility of leaching the element forms from the solid samples of vanadium slag and slime using 0.1 M solutions of Na<sub>2</sub>CO<sub>3</sub> and a mobile phase for the reverse-phase high performance liquid chromatography (RP HPLC) is studied. The compounds of vanadium are quantitatively recovered by both reagents, while for manganese compounds the extraction degree ranges within 1 – 10%. A mismatch in the retention time is observed upon the chromatographic separation of V and Fe forms in the model mixtures and in the resulting solutions after chemical processing of vanadium slag and slime.

**Keywords:** vanadium slag; vanadium slime; forms of the elements; microwave plasma atomic emission spectrometry; inductively coupled plasma mass spectrometry; sequential extraction procedure; reversed-phase chromatography; ion chromatography.

UDC 546.145:543.544.6

**Ion Chromatographic Analysis of Tape and Waste Water for Cation and Anion Content**

*Kolesnikov A. V., Kovalev E. V., Kovaleva A. Yu.*

Optimization of a chromatograph operation (850 Professional IC, Metrohm) is studied in analysis of drinking and wastewater for chlorine, fluoride, nitrite, nitrate and sulfate anions and cations of potassium, sodium and ammonium. It is shown that the correlation coefficient of the graphs plotted for the merged standard solution is closer to unity than that obtained for separate solutions of state standard reference samples. For each ion optimal conditions of calibration are specified. Optimal duration of the sample travelling through the analytical column and sample dosage are determined. The optimized method is used to obtain the chromatograms of standard solutions, drinking and wastewater. The results demonstrated satisfactory reproducibility and accuracy of analysis, as well as significant reduction of labor costs at a high efficiency of data accumulation.

**Keywords:** ions; chromatography; optimization; technique; cations; anions; drinking and waste water.

UDC 621.182

### Influence of the Operational Factors on the Structure of Tubing Coil Material of the Process Furnaces at Refineries

*Dobrovorskiy A. M., Maslikova E. I., Andreeva V. D.*

The impact of operational factors (long-term operation; standby modes; violation of technological regimes leading to the equipment failure) on the structure of internal and external surfaces of the furnace tubing coils made of chrome-molybdenum and chrome-nickel steels is considered. Attention is drawn to the non-uniformity of the structure in the cross-section of the coil. In addition to heat aging of the metal in pipes made of chrome-molybdenum steel upon operation at high temperatures and pressures, decarburization of inner and outer surfaces, as well as intergranular corrosion and in some cases formation of  $\sigma$ -phase are observed. The results of mechanical tests carried out on chrome-molybdenum steel of coils after their prolonged use and emergency cases are presented. The effects of  $\sigma$ -phase on the toughness, susceptibility to intergranular corrosion and residual life of coils made of austenitic chrome-nickel steels are considered. The fine structure and kinetics of  $\sigma$ -phase growth at operating temperatures of coils are refined. The obtained results show that despite the satisfactory mechanical properties final conclusion on the residual life of coils and the possibility of their further use can be made only with complete data on the metal structure throughout the whole cross-section of the tubes in hand. Evaluation of the residual life should be made with allowance for non-uniformity of the phase composition of the tube cross-section and corrosive damage present on the surface. Particular attention should be paid to identification of  $\sigma$ -phase in the structure, because even a small amount of  $\sigma$ -phase present at the grain boundaries can lead to a rapid embrittlement of metal. It is recommended to perform a laboratory metallographic study of the whole cross-section of the tube in addition to regular technical diagnostics of the furnace coils using methods of nondestructive control and mobile metallography.

**Keywords:** petrochemical equipment; residual life; decarbonized layer;  $\sigma$ -phase structure; toughness; intergranular corrosion.

UDC 536.631:620.19

### Study of the Heat Capacity of Coated Metal Materials Using Laser Flash Method

*Loshchinin Yu. V., Folomeykin Yu. I., Pakhomkin S. I.*

Results of laser flash measurements of the specific heat of the samples of metallic materials (stainless steel 12X18H9T, VZhM-4 nickel superalloy) coated with heat-resistant silicate enamel within a temperature range 20 – 1300 °C are presented. Within the specified temperature range the coating is characterized by high and constant emissivity close to 0.9. Comparative analysis of the measurement results and most reliable most reliable literature data revealed that a decrease in the apparent specific heat within the temperature range of 850 – 1100 °C is attributed to exothermic thermal effect. Deviation of the measurement results from the reference data is not more than 3 %. New data on the heat capacity of nickel superalloy VZhM-4 and temperature dependences of the apparent (with allowance for thermal effect of  $\gamma$ -phase dissolution) and true specific heat are presented. The discrepancy of calculated and measured values is below 2 %.

**Keywords:** specific heat capacity; thermal diffusivity; thermal conductivity; laser flash method; heat-resistant silicate enamel coating; adiabatic calorimeter; differential scanning calorimeter; emissivity of total radiation.

UDC 621.9

### Choice of the Effective Tool Material Proceeding from the Scribing Trace Parameters

*Mokritsky B. Y., Verkhoturov A. P., Pustovalov D. A., Vereshaka A. A., Evstigneev A. I., Kravchenko E. G.*

Determination of the operational properties of the metal-cutting tool through actual-service test is undesirable on virtue of long-duration and expensiveness of the testing procedure, especially when several tool materials to be compared are available in production or under development. Indirect methods of nondestructive control can provide a possibility of rapid (time-efficient) forecasting of the service properties or qualitative ranking of the materials to be compared by a certain service parameter. We have a good reason to believe that a method of pendulum scribing that comes most close (among all indentation-based procedures) to real conditions of tool loading upon cutting makes possible to get a trace on the sample or on the real tool resulting from interaction of the indenter with the studied material. The trace parameters can be considered a quantitative characteristic of the processes proceeding upon the specified interaction and can be used for forecasting of the operational properties of the tool material.

**Keywords:** performance evaluation; firmness period; crack resistance; pendulum scribing.

UDC 621.002.56;621.658.562;620.179.16.05

### Study of the Press-Fit Joints Using Multiangle Ultrasonic Sounding

*Ivannikov V. P., Kabakova A. V.*

A method of quantitative evaluation of the quality of press-fit joints using pulse-echo ultrasonic method is developed. It is shown that the reflection coefficient is the main parameter characterizing the quality of the press-fit joint, i.e., loading capacity determined by the maximum value of torque transmitted by press-fit joint, since it is attributed to normal stresses present at the joint surfaces. The equation based on the measured values of echo-pulse amplitudes in the quill cylinder and assembled joint is derived to calculate the coefficient of ultrasound reflection from the joint interference. Features of the research procedure are specified and described to provide reliable estimation of the quality of press-fit joints either of the selected area of the interference or the averaged around the joint estimation of the joint quality upon multi-

angle study of the object in different directions and present plane of ultrasonic sounding. An emphasis is made on the possibility and expediency of automation of the multiangle ultrasonic sounding control order to optimize the process of the joint quality assessing.

**Keywords:** press-fit joints; ultrasonic echo-pulse method; reflection coefficient; multi-angle ultrasonic sounding

UDC 620.178.3:539.4:621.773.9

### The Effects of Elastoplastic Deformation and Creep in Threaded Connections

*Makhtov N. A., Zatsarimiyi V. V.*

The specificity of loading conditions responsible for threaded connections of power equipment is demonstrated. Different approaches to the determination of their stress-strain states, attributed to a redistribution of stresses and strains in the threads under static and low-cycle loading are considered. The developed technique of experimental study of plastic deformation and creep deformation of studs at normal temperatures provides determination of the tightness reduction in studs.

**Keywords:** threaded connection; static and cyclic loading; elastoplastic strain; creep; loss of tightness.

UDC 620.169.1:620.17:621.773.9

### Static, Dynamic, and Cyclic Mechanical Strength of Studs of Large Hydraulic Turbine

*Matyunin V. M., Orachelashvili B. M., Marchenkov A. Yu., Kazantsev A. G., Kahadze M. Zh.*

The microstructure and mechanical properties of metal studs (steel 40Kh) M90×4 used for fixing the covers of large hydroelectric generating units are studied. The mechanical properties are determined in static, dynamic and cyclic tests of the samples cut out of the studs in longitudinal and transverse directions and at different distances from the surface. The character of changes in the microstructure and mechanical properties over the cross section of the stud is revealed. Static and cyclic tests of model and full-scale studs with nuts provide determination of the load and stress values responsible for the chain cut of turns of the threaded connection. Rather strong impact of the scale factor on the durability of studs under cyclic testing is disclosed.

**Keywords:** mechanical characteristics; microstructure; metal's strength; dynamical crack resistance; longevity; scale effect.

UDC 620.163.4

### The Impact Strength Prediction within a Transition Temperatures Range

*Baron A. A., Kunavin S. A.*

A method of accelerated evaluation of the impact strength  $KCV$  in the brittle-ductile transition range is developed. The unified impact strength diagram for steels is obtained. A unified linear relationship  $KCV_T$  over  $KCV_p = f\left(\frac{KCV_T HB_p}{KCV_p HB_T}\right)$  is derived

within a temperature range of 77 – 473 K where the subscripts "T" and "p" correspond, respectively, to the temperature at which the impact strength is to be determined and temperature that makes the Peierls-Nabarro plastic strain mechanism not valid any more. The procedure of the impact strength determination using the unified diagram thus obtained is described. The method provides reduction of the bulk of necessary tests without any significant damage to the reliability, and in some cases even to receive information inaccessible earlier because of the limited bulk of material.

**Keywords:** impact strength; Brinell hardness; brittle-ductile transition range.

UDC 620.178.152.2

### Determination of the Strain Character and Hardening of the Surface with Nano-Coating

*Skoblo T. S., Romanyuk S. P., Belkin E. L.*

Nanocoatings of CrN and WC are used to harden a cutting tool used in the processing industry. A method describing the imprint formation upon indentation of nanocoatings and character of deformation around them is developed. Mathematical processing of images obtained upon microhardness measurements revealed zones of plastic deformation around the imprint of the indenter in the material without coating. Coating of the disk knife surface increases hardness, thus preventing plastic deformation. Comparative study of nano- and microhardness demonstrated the possibility of reliable evaluation of the microhardness of the coatings at different loads and challenges in the measuring process.

**Keywords:** mathematical method; cutting tools; nanocoating; microhardness; plastic deformation.

UDC 620.178.16:621.793.7

### Enhance in the Quality of the Friction Surfaces of the Parts of Electric Pumps

*Poletaev V. A., Puchkov P. V.*

Most failures of the motors and pumps fail are attributed to wear of the loaded parts (shafts, bushings, etc.) due to their contact with rubber bearings and fluid passing through the pump elements. The aforementioned parts are made mostly of expensive steels 40Kh13 and 12X18H10T. It appeared impossible to improve the quality of the surface of the parts made of those steels by alloying or heat treatment. Therefore we propose to use steel 45 which is rather cheap and improve the quality of friction surfaces by hardening treatment which includes coating of the parts with chromium and ultra-diamonds, followed by subsequent turning and diamond smoothing of the surface.

**Keywords:** hardening; coating; hardness; roughness; surface quality; wear, ultra-diamond.