

However, a recent NMR study of ^{51}V showed that vanadium has two positions, V^{4+} and V^{5+} , below 35 K [10], i.e., charge ordering takes place. The theoretical consideration of the Coulomb repulsion between the electrons results in a linear (along the b -axis) ordering in the V^{4+} and V^{5+} chains, similar to a scheme suggested in Ref. [11]. However, the interaction with lattice deformations can make zigzag charge ordering more advantageous [12]. The simultaneous consideration of the Coulomb, electron – phonon, and spin – phonon interactions results in a great variety of types of charge ordering, depending on the relative magnitudes of these interactions [13]. What variant is realized upon the phase transition in NaV_2O_5 crystals remains to be answered in further experiments. The results of our recent study of the dielectric anomaly observed in the microwave and IR regions upon the phase transition in NaV_2O_5 suggest the presence of antiferroelectric ordering [14].

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New developments of optical spectral instruments in the Institute of Spectroscopy, RAS

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In a report presented in 1993, new supersensitive methods and optical spectral instruments developed in the Institute of Spectroscopy, RAS, and their applications in high technologies and ecology were discussed. Now, we consider new results obtained by means of these methods.

We consider briefly the results obtained by the method of laser atomic fluorescence spectrometry suggested and

developed by M A Bol'shov, V G Koloshnikov, A V Zybin, and S N Rudnev and LAFAS spectrometers with electrothermal atomization of a substance based on this principle. The direct analysis of ice samples in the Antarctic and the Northern Hemisphere aimed to study global changes in the climate and the consequences of practical activities of human beings gave new impressive detection limits for Cd, Bi, and Pb at a level of 3.6–0.2 fg (0.18–0.01 ppt). In collaboration with French researchers, the concentration of Cd was measured in the Antarctic ices depending on their age and its correlation with changes in the Earth's climate over the last 155 thousands years was monitored. Similar measurements were also performed for snow and ice in the Northern Hemisphere. It was found that at least 95% of the cadmium in layers up to 30 years old were of an anthropogenic nature.

Another supersensitive method for detecting elements is multistep resonance photoionization of atoms suggested by V S Letokhov and then developed by V I Mishin, G I Bekov, and Yu A Kudryavtsev. This method was recently used most successfully for studies in the field of laser-nuclear spectroscopy. The impressive feature of this method, provided the ionization is performed in a hot cavity or capillary, is the extremely high chemical selectivity, which is sufficient for suppression of the isobaric background, and the high ionization efficiency, which was successfully demonstrated many times on the ISOLDE accelerator with a mass separator (CERN).

An ion source producing ions selected over Z is based on laser ionization of atoms with short-lived nuclei in a capillary, which are formed in targets upon their bombardment by proton beams. This source consists of 1–2 copper vapor lasers with a total output power of up to 55 W, 2–3 dye lasers (above 1 W), and a nonlinear frequency converter (above 100 mW). The radiation from lasers tuned to the resonance transitions of isotopes under study passes through the window of a magnet of a mass separator and is focused at a distance of about 20 m onto the input aperture of a capillary. The capillary is usually a cylinder made of a high-melting metal with channels in its walls for the diffusion of products of nuclear reactions produced on the target.

The method of a laser ion source has recently been applied for producing chemically selective Mn ion beams for Mössbauer experiments, obtaining a neutron deficient Sn-101 isotope and long-lived Ni isotopes, for studying their energy spectra, producing beams of Ag, Be, Zn, Cd, and Cu, as well as, in problems of the materials technology, astrophysics, and nuclear physics. A recent achievement was the discovery and study by V I Mishin and V N Fedoseev in collaboration with ISOLDE of a strongly neutron excess silver isotope Ag-129, which is one of the key isotopes involved in the r -process proceeding inside stars and is responsible for the synthesis of heavy elements in the Universe.

In 1998, the Institute finished the development of a completely automated laser ion source intended for the same aims of laser-nuclear spectroscopy. All the components of this sophisticated laser complex — dye lasers with fast precision wavelength tuning, a portable precision wavemeter, a precision two-coordinate beam director, a spectrum analyzer, and a system of ion current detection, were improved over many years and represent completed instruments produced (it is important) by the Pilot Production Division of the Institute of Spectroscopy, RAS.

In the last five years, because of poor financing the main attention in laboratories has been devoted to the maintenance of unique spectrometers in a working state and to the development of portable spectral instruments.

Some resources have been concentrated on the improvement of a portable express analyzer of metals and alloys initiated by S L Mandel'shtam and developed by A M Livshits' group. At present, this instrument, based on emission spectral analysis, can detect more than 20 chemical elements in virtually all metal alloys and classify the alloys according to their types. The range of measurements of concentrations of elements is from 0.01 to 15% and the accuracy of measurements is 8–10%. The instrument weighs 15 kg and measures $500 \times 300 \times 300$ mm. An important advantage of the analyzer compared to expensive foreign analogs is the independence of the results of measurements from the environment and a superior resolving power. More than 20 such analyzers have been produced and are being successfully used in many plants in Russia. The basic elements of the analyzer of metal alloys are also used in other emission spectrometers based on an ICP source and a plasmotron for the quantitative analysis of complex compounds with higher concentration sensitivity to $10^{-4}\%$.

In most spectrometers and spectrum analyzers, optical signals are detected with multichannel optical spectrum detectors (MOSD) developed by É G Sil'kis and A V Peleznev on the basis of the CCD linear photodetectors or a set of linear arrays in the form of photoelectronic cassettes, which are also suggested for the replacement of photographic plates in standard emission DFS spectrometers and MFS polychromators. More than ten modifications of MOSD are being produced for the detection of extended spectra, long accumulation of weak signals, detection of pulsed signals, with boards in a personal computer, etc. The field of application of MOSD is very broad. For example, they are used in instruments for clinical diagnostics of cancer, in mobile laser analyzers of soil, and in spectrometers with an inductively coupled plasma. More than 20 multichannel detectors are used in research laboratories of institutes of RAS and institutions of the Ministry of Higher Education.

Another field is the development of a series of inexpensive, versatile Fourier spectrometers operating in the spectral range from 400 to 4000 cm^{-1} .

V M Krivtsun and N Yu Boldyrev suggested the design of such instruments implying a maximum avoidance of expensive precision and mechanical and optical elements by using electromechanical monitoring systems and computer technology. The optical scheme includes a high-quality, wide-aperture Michelson interferometer with a movable reflector. A stabilized He-Ne laser provides accuracy of measurement of wave numbers. The IR radiation is emitted by a global and detected either with a pyroelectric detector or a fast detector based on ternary compounds. It is also possible to measure both absorption and emission spectra from an external source.

The instrument can be readily coupled with different devices and attachments. It is characterized by good (for small-sized instruments) resolution (from 8 to 0.25 cm^{-1}) and a high signal-to-noise ratio (up to 3000 per scan at a resolution of 4 cm^{-1}). The spectrometer measures $460 \times 380 \times 200$ mm and weighs 18 kg. The first demonstration of operation of the Fourier spectrometer was its use for analysis of the content of CO in the air and of flour. The instrument is not inferior in its class and parameters to foreign

analogs, but is several times cheaper, even in the case of small-scale production.

Another strong instrument making group (A M Pyndyk, V N Krashennnikov, N I Ulitskiĭ, and V P Vinogradov), is engaged in the development of small spectral instruments in the visible and near UV and IR spectral ranges, which can be readily adapted for a specific spectral problem, and simultaneously in the development of a versatile laboratory high-resolution spectrometer for recording emission spectra, Raman and luminescence spectra.

The first line of investigation is represented by three basic models MS75, MS150, and MS300 with focal distances 75, 150, and 300 mm, respectively. The spectrometers are based on a vertical symmetric Ebert scheme, which is characterized by a low level of stray light and compactness. The reciprocal dispersion is in the range from 20 to 1.7 nm mm^{-1} , and the instrumental function of the spectrometer is not worse than $30\text{ }\mu\text{m}$.

An MS300 spectrometer with a CCD linear array (3600 pixels) was used for detection of the luminescence spectra of 3,4-benzpyrene in n-octane at liquid nitrogen temperature. An MS150 spectrometer equipped with a multichannel detector based on an image intensifier and supersilicon was used for detection of the concentration of (UO_2^{2+}) in water from its luminescence spectra. Both spectrometers were used in combination with holographic filters or a double monochromator with dispersion subtraction for detection of Raman spectra. Due to their compactness, low weight, and low energy consumption, these instruments can be used in the field.

A second line of investigation is represented by a versatile MS600 laboratory spectrometer with a focal distance from 600 to 1000 mm, a reciprocal dispersion from 0.45 to 2.5 nm mm^{-1} , and a relative aperture $1/5$. The spectrometer is used in a combination with a double monochromator with dispersion subtraction for detection of Raman and luminescence spectra of strongly scattering samples. Transmission of such a triple monochromator is 5–7%, however, the stray light does not exceed 10^{-10} .

A new line of investigation in the Institute is the development of a compact dichrometer for the rapid, highly sensitive detection of biologically active substances in biological liquids. The fundamental novelty of this instrument consists in the use of highly sensitive biosensors based on liquid-crystal dispersions of nucleic acids (DNA) or their complexes, whose chirality strongly increases upon interaction with biological structures and biomolecules, and in the measurement of the anomalous activity generated by biosensors at different wavelengths using the modulation technique.

The use of such biosensors developed by Yu M Evdokimov in the Institute of Molecular Biology, RAS, and also a number of optical and design solutions suggested by E L Mikhailov's group in the Institute of Spectroscopy, RAS, made it possible to simplify substantially the optical instrument, retaining its high sensitivity, and to make it more compact, more rapid, and less expensive compared to foreign dichrographs. The latest model of the instrument, with the use of foreign elements, measures $500 \times 340 \times 170$ mm, weighs 14 kg, and is computer-controlled. The dichrometer was used for the determination of very low concentrations of modern anticancer drugs (mitoxanthrone, etc.) in human blood and showed a detection limit of $2 \times 10^{-8}M$. This opens up the possibility for the successful development of a modern analytic test-system for biochemistry, medicine, and ecology.

The development of scientific instruments is an expensive and not always rewarding occupation, although new scientific results, especially in the fundamental aspect, can probably be obtained using only new instruments rather than commercial ones. For this reason, the Institute of Spectroscopy, RAS tries to support, despite many difficulties, the traditions of scientific instrument making and the activity of Pilot Production Division.