A new methodology for studies of fundamental processes in graphite furnaces, based on a combination of the Laser-Induced Fluorescence in Graphite Furnace (LIF GF) technique and a Variable-Pressure Atomizer (VPA), has been scrutinized. While the VPA, with its ability to provide a wide range of buffer gas pressures (P), allows for a separation of overlapping atomization processes, the LIF technique, with its high sensitivity, makes studies under analytical conditions (low analyte mass) possible.

Studies of evaporation and atomization phenomena of Ga and In atoms have been performed with this technique. It was found that the atomization efficiency and atomization mechanisms for Ga and In is dependent of P. For Ga at low P single first order atomization process with an activation energy (E_a), which is close to the energy of Ga evaporation, was obtained. At higher P, there is evidence of additional, high-temperature atomization process. With use of VPA it was possible to separate the low- and high-temperature processes and to estimate their parameters. It was shown that the mechanisms of Ga atomization include evaporation of Ga atoms from Ga clusters on the graphite surface—this mechanism dominates at low pressures— and collisional dissociation of Ga_2O molecules in gas phase, effective at high P.

For In, the nonlinear pressure dependence of the analytical signal also indicates the existence of some atomization processes, which characteristics were estimated. It was found that the E_a values depend on pressure, heating rate and sample mass. The possible mechanisms of In atomization in GF are discussed.

With use of this technique the matrix influences in wide range of pressures were studied. It was found that KCl and CuCl_2 matrices change the the pressure dependence of analytical signals as well as mechanisms of Ga and In atomization in different ways. In In+KCl system the atomization process due to collisional dissociation of InCl molecules in gas phase was obtained. In In+CuCl_2 system the surface reactions are more important. It was found that suppression of the analytical In signal has different P-dependencies for these two matrices. In the presence of KCl the suppression increases as P decreases, while an opposite behavior holds in the presence of the CuCl_2 matrix. The future prospects of the approach are discussed.

**INVESTIGATION OF DIFFERENT DETECTION SCHEMES FROM TRACE Rb DETERMINATION IN GRAPHITE FURNACE BY AAS WITH WAVELENGTH-MODULATED DIODE LASER**

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**Atomic absorption, trace element analysis, diode lasers, wavelength modulation, Rb**

Wavelength Modulation Diode Laser Absorption Spectrometry (WM-DLAS) is nowadays a useful technique for sensitive detection of atomic and molecular species under a variety of conditions. The important feature of LAAS DL technique is the possibilities of fast tuning of
laser wavelength that allows using a modulation technique and decreasing so the limit of detection more than 100 times.

A drawback with the WMAS technique is, however, that various types of background signals often limit the detectability. It is extremely important for GF with fast heating. In order to detect as low concentrations as possible of a specific type of species, it is of importance to characterize these so appropriate measures for their reduction or elimination can be made for each specific application.

The main goal of this work is to study the new approaches to decrease the magnitudes and fluctuations of background signals and to obtain the optimal conditions of atoms determination by the WM-DLAS technique in a graphite furnace (GF). Of special importance in this work has been to investigate the use of different detection schemes (in particular detection at the 2nd, 4th, and 6th harmonics of the modulation frequency) to deal with the existence of etalons from windows in a GF. A number of experiments in which these harmonics have been detected simultaneously for a variety of furnace conditions have been performed. The furnace has been equipped alternatively with and without windows. The work has thus consisted of measurements and analysis of background signals from various experimental set-ups as well as an investigation of the detectability of low amount of Rb. The measurements were done for Rb concentrations in the low ppt-range. Detection of Rb has been performed with both a window-equipped and an open GF in low fg and sub-fg amounts. New and improved detection limits are reported.

The multichannel version of this technique was used to study of spatial distribution of Rb atoms in GF with and without matrices. It was found that for Rb atom this distribution is nonhomogenous as well as the suppression of the signals by matrix. The optimal conditions of Rb determination in different matrices with use of narrow laser beams were found.

**ROUTINE X-RAY FLUORESCENCE ANALYSIS OF THE POWDER MATERIALS BY “VERBA-XRF” MODE**

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**Key word: X-ray spectrometry, analysis, VERBA-XRF, powder material, clay, clinker, gypsum, slag (dross), schlamm.**

New version of the “VERBA-XRF” Mode [1] is applied first time. X-ray spectrometer register only the analytical lines of principal chemical elements, which have atomic number $Z > 10$. The complementary chemical elements have atomic number $Z < 9$.

We developed mathematical model, which calculate the content of each principal chemical element and content sum of the complementary chemical elements. In addition, it is realize full correction of the interelement influence and background. The element contents are not normalized to 100 %, because “VERBA-XRF” mode does not allow it.

The content of 8 principal chemical elements, viz., Fe, Ti, Ca, K, S, Si, Al, Mg, and content sum of the complementary chemical elements were determined. We analyzed 120 samples: dust from electric filter, clay, clinker, gypsum, bauxite, slag (dross), candle-end, shale (schist), schlamm, chalk. Each sample contains oxygen, nitrogen, carbon and hydrogen as complementary elements in unlimited quantities.

Multichannel X-ray spectrometer SRM-25 (anode - Rh, voltage - 50 kV) registered the intensities of 8 analytical lines of the principal elements. Powdery samples (with the grains sifted by a 74-mm sieve) were pressed into tablets.