Publ. Astron. Obs. Belgrade No. 84 (2008), 431 - 434 *Contributed Paper*

PULSED DISCHARGE IN COMBINED HOLLOW CATHODE AS SOURCE FOR ANALYTICAL GD TOFMS. DYNAMIC DISCRIMINATION OF CLUSTERS AND DISCHARGE GAS IONS IN AFTERGLOW

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Abstract. Some dynamic processes in pulsed discharge in combined hollow cathode used as source for analytical GD TOFMS are considered. The effect of the addition of hydrogen to glow discharge coupled to a time of flight mass spectrometer has been studied. Addition of hydrogen has shown the increase intensities of sample components and decrease intensities of discharge gas components. Reactions describing processes at presence of hydrogen are considered. Influence of pressure on discharge gas and dynamic of clusters transportation on intensities of clusters components was investigated for some types of clusters. Dynamic discrimination has allowed to increases number of determined elements due to essential reduction of interferences.

1. LOW TEMPERATURE PLASMAS

1. 1. PLASMA APPLICATIONS AND DEVICES

Some types of glow discharge are used as sources coupled with mass-spectrometry for solid, bulk samples analysis and thin-layer determinations. These sources work with direct current (DC), magnetron, radiofrequency (RF) and pulsed discharges. High sputtering and ionization efficiency for pulsed discharge increase sensitivity, asymmetric origin of analyte and discharge gas ions allowing reduce background gas contribution, perturbation of chemical system, followed by different relaxation effects – for example dissociation and recombination of different molecular ions in afterglow, selective reactions between molecular ions and Hydrogen etc. These effects can be used in analytical GD TOFMS system for effective background discrimination. Besides pulsed glow discharge reduce average of discharge power and cathode temperature under high pulsed power. Pulsed discharge in combined hollow cathode (CHC) (see

Ganeev et al. 2007) has a side benefit (compare with Grimm pulsed discharge) – it allowing analyse, as RF discharge, dielectric and semi-conducting samples.

In the glow discharges some types of clusters are generated in afterglow and consequently well known problem of occurrence interferences in clusters and sample components. For pulsed discharge intensities of some clusters can be decreased in high degree by optimization of two parameters - pressure and repelling pulse delay τ_d. Influence of pressure on discharge gas and dynamic of clusters transportation on intensities of clusters components was investigated for three types of clusters: Hydroxyls, MOH^+, MOH_2^+ ($SiOH^+$, $CuOH^+$, $CuOH_2^+$, etc.); symmetric ionic molecules of matrix element: $MiMj^+$ ($^{63}Cu^{63}Cu^+$, $^{63}Cu^{65}Cu^+$, $^{65}Cu^{65}Cu^+$, $^{28}Si_2^+$) and Argides: MAr^+ ($SiAr^+$, $NiAr^+$, $CuAr^+$).

In experiment CHC TOFMS system (Lumas-30) was used. It was found that as the pressure as repelling pulse delay increasing decreases relative intensities of first two types of clusters in high degree. This effect can be explained by clusters dissociation in collisions with neutrals in afterglow. Let's note that the effect of clusters temporal discrimination is feebly marked for argides. Probably dissociation energies for argides is appreciable higher than the energies for others types of clusters. Besides clusters dissociation, ion-electron recombination can play essential part in decreasing of relative clusters intensities when repelling pulse delay and pressure increases.

2. EFFECT OF HYDROGEN ON MASS SPECTRA

It was shown that hydrogen (1-20%) in direct current GD significantly decreases intensity of such spectra components as Ar^+, H_2O^+, H_3O^+, ArH^+ and increases intensity of Cu^+ in 6 times (see Saito, 1997). The increasing of sample elements intensities under the same conditions was reported in the same paper. Various effects connected with nonconductive sample ions sensitivities were reported for RF GD source (see Tanaka, et al. 1996).

In this work the experiments with a gas mixture containing hydrogen in pulsed discharge in hollow cathode are described. The copper standard 9410 was used. It is found that intensities for Sb^+, Ag^+, Cu^+ are not appreciably changed, in contrast to the results reported in (see Tanaka, 1996). More significant changes can be noted for Al (its intensity decreases approximately in 2 times) and Pb (its intensity increases in 1.5 times). At the same time intensities of gas components (Ar^+, OH^+, H_2O^+, H_3O^+, ArH^+) were reduced in many times (20-100) in the presence of hydrogen, that is consistent with (see R.S.Mason et al. 1997). These changes are illustrated in Fig. 1 where spectra of copper standard sample N 9410 without Hydrogen (Fig. 1a) and with 0.5% Hydrogen (Fig. 1b) are presented. It can be seen from the figure that the presence of hydrogen appreciably decreases intensity of gas components in mass spectrum (Ar decrease in 10^4 times, ArH – in 10^3 times, OH, OH_2 – in 10^2 times). It significantly reduces an interference of gas components and sample elements, especially for light elements.

However in the presence of relatively high hydrogen concentration (5-15%) miscellaneous clusters were observed in spectra, for example, $CuArH^+$, $CuAlH^+$, $CuOH_2^+$, $CuOH_3^+$, $Al_2O_3H^+$ and others. Although theirs intensities were lower than basic spectra components on 5-6 degrees, their presence significantly decreases analytical performance of the mass-spectrometer. As a result in further experiments the gas mixture with relatively low hydrogen concentration (0.3%) was used. In this case

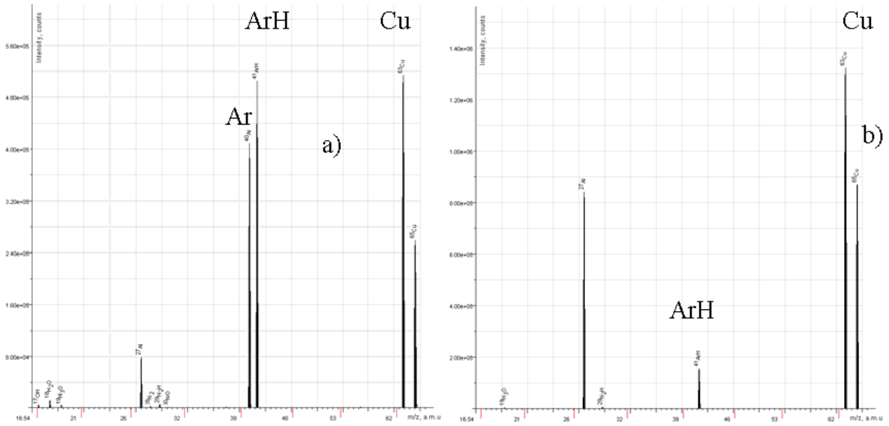

Figure 1:

a significant suppress of gas components is observed and at the same time hydride clusters are practically absent.

Mechanism of hydrogen influence on mass-spectrum components is not clear until now. Attempts to explain this phenomenon were undertaken in (see Newmann et al. 2004). Increase of metastable Ar atoms due to quenching of higher resonant levels by H_2 is suggested in (see Mason 1997), Rydberg Ar atoms production mechanism leading to interactions with H_2 is considered in (see Newmann et al. 2004). Apparently the suggested explanation are valid only for direct current glow discharge (namely this discharge type was used in these works). At the same time increase intensities of sample components and decrease intensities of gas components are more universal phenomena because they are observed in radiofrequency discharge (see Tanaka et al. 1996) and in our case in pulsed glow discharge.

It's necessary to note that addition of Hydrogen in discharge gas in pulsed discharge leads to occurrence in a spectrum of such components as H_4^+ and even H_5^+ (see Fig. 2). Presence of these a component follows from the equations for the basic reactions in glow discharge at presence of hydrogen.

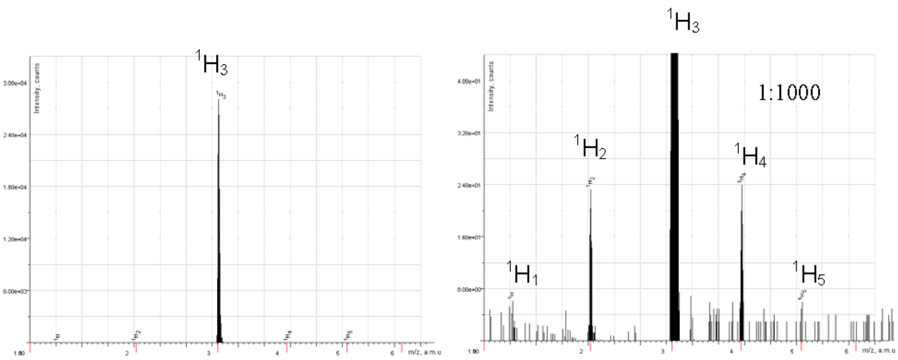

Figure 2:

These reactions are presented below:

$$\begin{gathered} Ar^+ + H_2\text{–}\ ArH^+ + H \\ ArH^+ + H_2\text{–}\ Ar + H_3^+ \\ OH^+ + H_2\ \text{–}\ OH_2^+ + H \\ OH_2^+ + H_2\text{-}\ OH_3^+ + H \\ H_2^+ + H_2 - -H_3^+ + H \\ H_3^+ + H_2 - -H_4^+ + H \\ H_4^+ + H_2 - -H_5^+ + H \\ COH^+ + H_2\text{–}\ COH_2^+ + H \\ Cu + OH+ \text{ - } CuAr^+ + e \\ Cu + Ar^* \text{ - } CuAr^+ + e \\ ArH^+ + e - -Ar + H + e \end{gathered} \tag{1}$$

$$\begin{gathered} CuAr^+ + H_2\text{–}\ CuArH^+ + H \\ CuArH^+ + H_2 - -\ CuArH_2^+ + H \end{gathered} \tag{2}$$

These processes rapidly increase Ar^+ and other atom's ions recombination rate because cross-sections of molecules recombination are much higher than cross-sections of atoms recombination, even if we assume three-body, radiative or other atoms direct recombination mechanisms. We suggest that these processes also significantly increase recombination rates of molecular and atom gas components like Ar, OH, OH_2, CO, CO_2, N_2, etc in afterglow. Increase in intensities of metals ions in presence of in presence of hydrogen may be explained by increase of metastable Ar and H atoms owing to process (1) and thus by increase of Penning ionization rate. Penning ionization is a nonselective process but it can ionize only atoms or molecules that have ionization energy less than Ar or H excitation energy. This condition is valid for the large majority of metals. Other gas compounds in the discharge (molecules) have higher ionization energy (10-13 eV). Hence only intensities for several metals are (slightly) increased which is proved by our measurements. It is significant that metals ions can not take part in reactions (1) because ionization energies of majority of metals ($6 - 9$ eV) are less than the first excitation potential of hydrogen (10.2 eV). In this case a potential barrier of 3-6 eV prevents reactions (1). Therefore presence of hydrogen in the discharge does not reduce the intensities of sample components.

Dynamic discrimination allowing determines some element in different types of samples despite the presence of interference. For example spectra of cleared and metallurgical Silicon are shown on Fig. 3. As one can see ^{40}Ca in metallurgical Silicon does not interfere with ^{40}Ar because intensity of ^{40}Ar is very low.

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