

Laser-induced electron transfer desorption/ionization of metal complexes on TiO₂ films

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Abstract. Thin titanium dioxide (TiO₂) films were studied as ion emitters for the laser-induced electron transfer desorption/ionization (LETDI) of metal complexes with organic reagents. The TiO₂ films (350 nm thick) were deposited on the silicon substrates by e-beam evaporation of TiO₂ powder. Copper complex with phthalocyanine, rhenium complex with thiocarbanilide and platinum complex with 8-quinolinethiol were studied as the test analytes. Reflectron time-of-flight mass spectrometer with the rotating ball interface was used for analysis. The analytes were applied on the surface of TiO₂ film using an electrospray deposition. All tested compounds are detected as the radical molecular ions with no fragmentation. It is found, that TiO₂ films are very stable and show good sensitivity in examined range of the analyte concentrations. The limits of detection of studied complexes were at the subfemtomole range, and the relative standard deviation was less than 10%.

1. Introduction

The analytical interest in metal-organic complexes arise from their potential use in a variety of applications of these complexes e.g. in the field of industrial photocatalysis, artificial photosynthesis, light-activated pharmaceuticals and highly efficient separation and preconcentration of metal element traces. Traditionally, investigations of such complexes have predominantly been performed using various spectroscopy methods, such as UV/visible, electron paramagnetic resonance and nuclear magnetic resonance spectroscopy. The limits of detection of spectrophotometric methods are usually at a level of not lower than 1 picomole of substance in the sample. Very few studies have employed more sensitive and specific mass-spectrometric techniques.

Recently, we introduced Laser-induced Electron Transfer Desorption/Ionization (LETDI) [1], a novel variant of Surface Assisted Laser Desorption/Ionization (SALDI) method. In SALDI, the ionized species are formed from analytes deposited on a surface of specially designed substrate, an ion emitter, which is irradiated with a laser beam at a wavelength well absorbed by the substrate [2]. The



most commonly used material for SALDI is silicon, in particular, porous silicon [3], ordered nanocavity arrays [4] and amorphous silicon [5,6]. Most reported results on silicon based SALDI were obtained with basic compounds, which are detected as protonated molecules. In this case, only compounds with relatively high basicity in a gas phase (higher than 820 kJ/mol) are efficiently ionized [7]. Many important transition metal complexes have values of basicity much lower than 820 kJ/mol; therefore, they are not observed as protonated molecules by conventional SALDI. In LETDI, both substrate and analyte molecules absorb the laser radiation. This provides another mechanism for ionization of chemical compounds which is based on an electron transfer from the excited adsorbed analyte molecule to the semiconductor material. In contrast to a regular SALDI approach, chemical compounds with low basicity could be ionized by LETDI.

The previously reported results on LETDI mass spectrometry of metal complexes were obtained with silicon substrates [1,8]. In this work the titanium dioxide TiO_2 films were developed as ion emitters for the laser-induced electron transfer desorption/ionization of metal complexes. Rhenium (Re), platinum (Pt) and copper (Cu) complexes with common organic reagents were studied as test analytes.

2. Experimental

A schematic of the experimental setup is shown in figure 1.

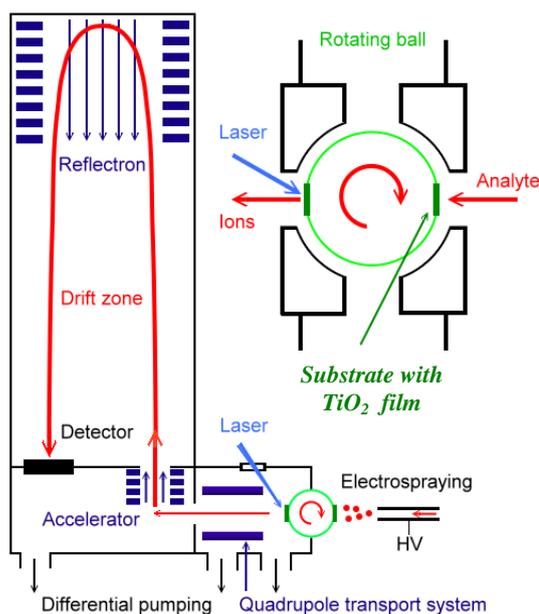


Figure 1. Schematic of the experimental setup. The instrument implements a combination of an ion source based on LETDI with a time of flight mass spectrometer. The inset shows a rotating ball interface.

The mass spectrometer was the time of flight reflectron with the orthogonal ion injection via gas-filled radiofrequency quadrupole (MX 5311, IAI of RAS, St. Petersburg). The rotating ball interface was used to couple the sample deposition chamber, where analytes were deposited on the semiconductor substrate, and the ion source, where the deposited analytes were ionized [9,10].

A diode-pumped YAG laser with near-diffraction limited beam quality, 0.35 ns pulse duration, was operated at 300 Hz. A frequency-tripling crystal yielded a 355 nm laser pulse of about 50 μJ . The laser pulse energy was varied in the range of 10-30 μJ using an attenuator. In order to more efficiently utilize the analyte, the laser focus was scanned over a $1 \times 2 \text{ mm}^2$ sample deposition area using a computer-controlled, dual-mirror scanner. The laser focus moved approximately 0.1 mm between successive laser shots, and about 300 individual mass spectra were obtained from different points on the probed area of the ion emitter and were accumulated by the ADC digitizer during one "scanning cycle". The multiplier supply voltage was adjusted to provide a single-ion pulse from the ADC digitizer output that yielded an integrated signal equal to 1. Thus, the number of ions detected, for

example during one raster scan, was simply obtained by integrating the output signal. The overall number of detected ions for any peak in the mass spectrum, over any number of raster scans, was similarly obtained.

The titanium dioxide TiO₂ films were deposited on the monocrystalline silicon substrates by e-beam evaporation of TiO₂ powder (initial pressure of 7×10^{-4} Pa, working pressure of 3×10^{-3} Pa and deposition rate of 50 nm/min). The results of the ellipsometric and secondary electron microscopy studies of the TiO₂ films indicated a thickness of about 350 nm, refractive index of 2.167, and a smooth and uniform surface morphology. Two substrates were installed on opposite sides of the rotating ball (see figure 1). The analytes were applied on the surface of TiO₂ film using an electrospray deposition, the ball was rotated 180°, and the analytes were ionized and desorbed by laser irradiation for the subsequent mass spectrometric analysis. All measurements were performed in the positive ion detection mode.

Copper complex with phthalocyanine was obtained commercially.

Rhenium complex with thiocarbanilide (diphenylthiourea) was synthesized according to the known procedure [11].

Platinum complex with 8-quinolinethiol was synthesized by a reaction of H₂PtCl₆ with 8-mercaptoquinoline using the microwave system Discover SP-D (CEM, Matthews NC, USA). To 10 mL of Pt solution in 2M HCl was added 1 mL of a saturated solution of 8-mercaptoquinoline in ethyl alcohol. Then, the solution was heated in the microwave system to 80°C at a rate of 12 K/min and kept for 5 min at this temperature; thereafter, the solution was cooled to room temperature, and 2 mL of chloroform was added. The mixture was allowed to separate into layers, and a chloroform fraction was taken for further analysis.

The obtained complexes were characterized by ¹H-NMR and UV/visible spectroscopy.

3. Results and discussion

It was found that for achieving optimum sensitivity and mass spectral performance, the TiO₂ films must first be activated by irradiating the surface by UV laser pulses to remove the adsorbed molecules. Full activation requires several (up to 10) laser pulses on each substrate spot. Activation was performed before any analysis and without analyte.

The preliminary study of threshold behavior of TiO₂ films showed that 30 mJ/cm² of laser intensity gives the best performance for all studied analytes. Decreasing the laser fluence leads to the dramatic decreasing of the ion signal. With the increase of laser fluence titanium containing peaks appeared in mass spectra, indicating the destruction of the film. Therefore all following experiments were carried out at 30 mJ/cm² of laser fluence.

A LETDI mass spectrum of the Re complex with thiocarbanilide obtained from 10⁻⁶ M analyte solution is shown in figure 2. The mass spectrum reflects the isotopic cluster at mass-to-charge ratio *m/z* 657 for the most abundant peak, with no Re-containing fragment ions observed. It is well known that natural rhenium consists of two isotopes with masses of 185 Da and 187 Da having a ratio ¹⁸⁵Re/¹⁸⁷Re = 37.4/62.6. The characteristic Re isotope pattern considerably facilitates the identification of Re-containing ions. The measured *m/z* values, as well as the observed isotopic ratio, allow these peaks to be identified to correspond to the radical molecular ion isotopic cluster of the complex ReOL₂, where ligand L is (thiocarbanilide – H) SN₂C₁₃H₁₁ (structural formula of the complex is shown in the inset). Figure 3 compares the calculated and measured isotopic distribution of the molecular ion peak. It can be seen that the observed isotopic distribution agrees well with the theoretical spectra predicted for molecular radical cation (ReOL₂)⁺. Therefore, the main ionization channel of the Re complex is electron transfer from the test molecule. In addition to Re-containing peaks, K⁺ at *m/z* 39 and Na⁺ at *m/z* 23 ions are observed in mass spectrum.

LETDI mass spectrum of the Pt complex with 8-quinolinethiol obtained from 10⁻⁶ M analyte solution is shown in figure 4. The mass spectrum is dominated by the isotopic cluster at *m/z* 514 and *m/z* 515 for the most abundant peaks. No fragment ions were detected in the mass spectrum. Pt-

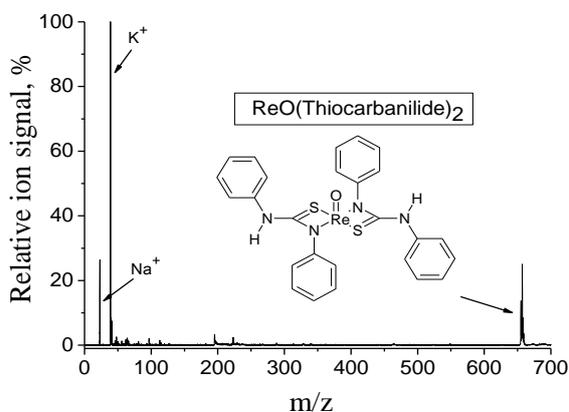


Figure 2. LETDI mass-spectrum of rhenium complex with thiocarbanilide.

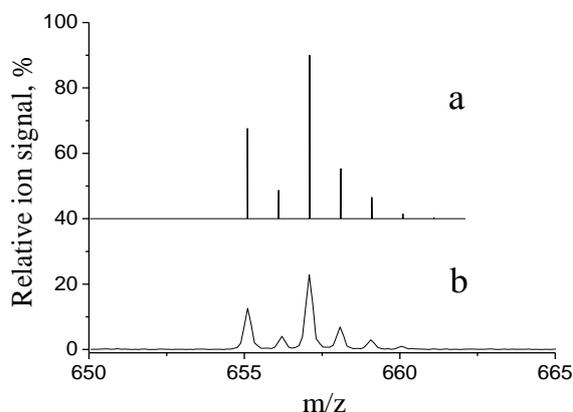


Figure 3. Calculated (a) and measured (b) isotopic distribution of the molecular ion peak $\text{ReO}(\text{thiocarbanilide})_2^+$.

containing peaks can be easily interpreted as the molecular ion isotopic cluster of the complex PtQ_2 , where ligand Q is (8-quinolinethiol – H) SNC_9H_6 (see inset of figure 4).

Figure 5 shows a LETDI mass spectrum of the Cu complex with phthalocyanine obtained from 10^{-6} M analyte solution. Similar to that of the Re and Pt complexes the molecular ion isotopic cluster at m/z 575 is observed in the mass spectrum, with no Cu-containing fragment ions detected. According to the mass spectrometric data Cu complex have composition Cu-Pht where ligand Pht is (phthalocyanine – 2H) $\text{C}_{32}\text{H}_{16}\text{N}_8$ (see inset of figure 5).

The obtained results demonstrate that LETDI on TiO_2 films is a soft ionization technique. LETDI mass spectra are “clean” with low chemical background except the peaks corresponding to the ions of sodium and potassium. However, peaks of these alkali metals are observed in the low-mass region and have not a considerable effect on the quality of the results obtained.

Additionally, experiments were carried out to compare the mass spectral characteristics of the TiO_2 films to the silicon substrates. Silicon substrates were produced inside the ion source of the mass spectrometer by repeated laser irradiation according to the early reported procedure [1]. LETDI mass spectra from Si substrates found to be similar to those produced with using TiO_2 films for all tested

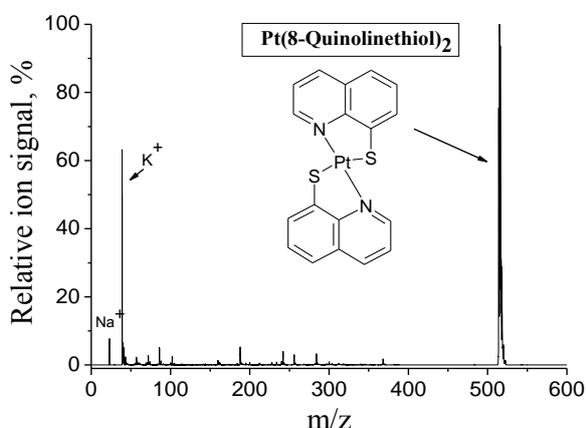


Figure 4. LETDI mass-spectrum of platinum complex with 8-quinolinethiol.

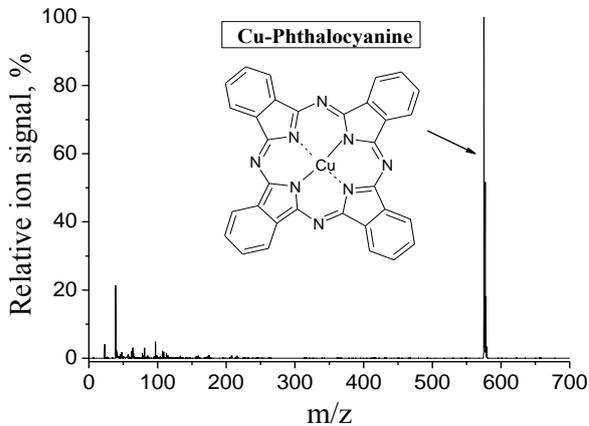


Figure 5. LETDI mass-spectrum of copper complex with phthalocyanine.

metal complexes. However, it was found that signal-to-noise ratio (S/N) obtained with using Si substrates was at least 2 times lower in comparison to S/N obtained with TiO₂ films. Another important advantage is that TiO₂ films are very stable under atmospheric conditions in contrast to Si substrates. There was no significant decrease in ionization efficiency after a few months storage of TiO₂ films in air. The surface of TiO₂ layer was not cleaned in any way, except by laser irradiation before the analysis.

To estimate the sensitivity and the limit of detection of investigated metal complexes the TiO₂ surface with known amount of deposited analyte was scanned several times until all the analyte signal vanished. The amount of analyte deposited was obtained simply from the analyte concentration, electrospray flow rate and the deposition time. The overall number of generated ions was obtained by integrating the output signal for all peaks corresponding to the metal complex including isotopes. From data obtained it was found that the limits of detection (i.e. the amount of sample needed to produce a spectrum with analyte signal-to-noise ratio $S/N \geq 3$) of studied complexes were at the subfemtomole range and the sensitivities were 20-100 ions/fmol.

The ions signal was measured for different amounts of analytes over a range of 3 orders of magnitude. The linearity of response was studied by varying the concentration of analyte solutions and the deposition time. The correlation coefficient found to be above 0.995. The relative standard deviation for five replicate analyses was less than 10%. A relatively high reproducibility is caused by several factors. Firstly, TiO₂ films were deposited using a highly reproducible method, resulting in uniformity over large areas and in high purity. Further, the surface was carefully cleaned before analyte deposition. Finally, with stable spray deposition, the rotating ball interface provided reproducible sample introduction.

The obtained results clearly demonstrate that TiO₂ films are applicable to the quantitative analysis of metal complexes with organic reagents by LETDI technique.

4. Conclusion

Thin titanium dioxide films obtained by e-beam evaporation of TiO₂ powder were investigated for the laser-induced electron transfer desorption/ionization (LETDI) of metal complexes with organic reagents. Copper complex with phthalocyanine, rhenium complex with thiocarbanilide and platinum complex with 8-quinolinethiol were studied as the test analytes. Reflectron time-of-flight mass spectrometer equipped with LETDI ion source and with the rotating ball interface was used for analysis of analyte solutions. Advantages of TiO₂ films application for LETDI of metal complexes are the following:

- high purity;
- easy and controllable method of fabrication;
- high uniformity over large areas;
- films can be deposited on any construction material;
- high stability of deposited films under atmospheric conditions;
- TiO₂ based LETDI ion source generates simple mass spectra of metal complexes, dominated by radical molecular ions. Mass spectra are "clean" with low chemical background;
- high ionization efficiencies and low limits of detection (at the subfemtomole range) of investigated metal complexes;
- chemical specificity;
- relatively high reproducibility;
- ability to analyze samples rapidly.

These advantages make TiO₂ films a potentially powerful tool for the detection of metal complexes and related compounds using LETDI technique.

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References

- [1] Grechnikov A, Nikiforov S, Strupat K and Makarov A 2013 *Anal. Bioanal. Chem.* **406** 3019
- [2] Alimpiev S S, Grechnikov A A, Sunner J, Karavanskii V A, Zhabin S N, Simanovsky Ya O and Nikiforov S M 2008 *J.Chem.Phys.* **128** 014711
- [3] Wei J, Buriak J M and Siuzdak G 1999 *Nature* **399** 243
- [4] Finkel N H, Prevo B G, Velez O D and He L 2005 *Anal. Chem.* **77** 1088
- [5] Alimpiev S S, Grechnikov A A, Sunner J, Borodkov A S, Karavanskii V A, Simanovsky Ya O and Nikiforov S M 2009 *Anal. Chem.* **81** 1255
- [6] Grechnikov A A, Borodkov A S, Alimpiev S S, Nikiforov SM, Simanovskii Ya O and Karavanskii VA 2010 *J. Anal. Chem.* **65** 1504
- [7] Grechnikov A A, Borodkov A S, Alimpiev S S, Nikiforov S M, Simanovsky Ya O 2013 *J. Anal. Chem.* **68** 19
- [8] Borisova L V, Borodkov A S, Grechnikov A A, Ugolkova E A and Minin V V 2013 *Russ. J. Inorg. Chem.* **58** 940
- [9] Alimpiev S S, Grechnikov A A, Sunner J, Karavanskii V A, Simanovsky Ya O and Nikiforov S M 2011 *Rapid Commun. Mass Spectrom.* **25** 140
- [10] Grechnikov A A, Kubasov A E, Georgieva V B, Borodkov A S, Nikiforov S M, Simanovsky Ya O and Alimpiev S S 2012 *J. Phys.: Conf. Ser.* **398** 012033
- [11] Borisova L V and Ermakov A N 1974 *Analytical chemistry of rhenium* (Moscow: Nauka).