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Matrix assisted laser desorption ionization (MALDI) and laser desorption ionization (LDI) mass spectrometry for trace uranium determination: The use of C_{60}-fullerene as a matrix

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The use of buckminsterfullerene (C_{60}) carbon clusters as a matrix for MALDI-TOFMS of uranium determination was studied. The C_{60} fullerene is easily ionized either to C_{60}^- or C_{60}^+ ions and when increasing the laser energy, the destruction of C_{60} to C_{58}, C_{56}, C_{54}, etc. fragments and the formation of higher carbon clusters C_{106}^+, C_{108}^+, C_{118}^+, etc. is observed. In the same time with the fullerene destruction, the intensity of uranium oxide peaks UO_2^+ and UO^+ is intensified. Conditions such as laser energy and the use of linear, reflectron, negative or positive modes were studied and the detection limit of uranium down to ~50 femto mol of uranium was reached.

Introduction

Uranium contamination due to mining and milling activities has extended to large regions localized in several countries around the world. Therefore, the potential migration of uranium and actinides in underground waters is of great concern and current environmental issue. Besides, risk assessment, especially serving nuclear waste management, is of prime importance. Another serious concern is environmental pollution with depleted uranium, especially in last battlefields where depleted uranium penetrators were used in large scale.[1,2]

For these reasons, sensitive methods for monitoring traces of uranium are needed. Fluorescence spectrometry, inductively coupled plasma atomic emission spectrometry with solvent extraction, X-ray fluorescence after preconcentration, etc. are among the most sensitive methods for trace uranium determination. Even so, new approaches and techniques are continuously searched for. In a previous work, we have shown that quantitative estimation of uranyl levels in waters can be done by MALDI-TOFMS.[1] However, it was found that the analysis is complicated by the formation of uranium–oxygen clusters, although they can be eliminated with the use of certain matrices.[2] This instrumentation can also, in some extent, be applied for speciation analysis.[3]

The aim of this paper was to investigate the possibility how to improve further the determination of uranium traces. Due to increasing importance and powerful characteristics of matrix-assisted laser desorption/ionization coupled with a time-of-flight mass spectrometer (MALDI-TOFMS),[4,5] the possibilities of this technique for the purpose of sensitive uranium determination were examined.

Experimental

Instrument

Mass spectra were collected on a Kratos Axima-CFR MALDI-TOF mass spectrometer (Manchester, U.K.) purchased from Shimadzu (Vienna, Austria). The spectrometer is equipped with a N_2 laser, operating at 337 nm. Spectra were recorded in linear and reflectron modes, either positive or negative. The laser power was used above the threshold of ion formation/desorption and higher. The laser power is given in arbitrary units (au). The full power of the laser is reached at 180 au.

Chemicals

Buckminsterfullerene (C_{60}) was purchased from Merck (Darmstadt, Germany). Toluene, and oxalic acid were from Lachema (Brno, Czech Republic). A mixture of C_{60} and C_{70} was either from Merck or kindly donated by Prof. Janča, Department of Physics, Masaryk University. 9-Nitroanthracene (9-NA) and 5-methoxysalicylic acid (5-MS) were from Aldrich (Milwaukee, USA). Uranyl nitrate ($UO_2(NO_3)_2 \cdot 6H_2O$) was from Lachema (Brno, Czech Republic) and diluted, 1 mM solution was prepared by double distilled water.

Results and discussion

In order to explore the utility of MALDI-TOFMS for the quantification of uranium traces, precision and accuracy of analysis using buckminsterfullerene, C_{60}, as analyte in MALDI-TOFMS, was also investigated.

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This part of the study was presented first because we wanted to test also the use of C_{60} as (1) internal standard for quantitative applications, and (2) as a matrix in MALDI processes of uranium determination.

Since C_{60} was attempted to use as a matrix, first MALDI-TOFMS of fullerenes was investigated in detail.

LDI time-of-flight mass spectrometry of fullerenes

The laser desorption/ionization (LDI) threshold for buckminsterfullerene (C_{60}) was found at 30 au. Below this threshold, no signal involving fullerenes was detected. At laser energy >30 au, the fullerenes can easily be ionized producing either cations or anions. An example of the negative-ion LDI-TOF mass spectrum (linear mode) obtained for a buckyball mixture (mainly C_{60}, C_{70} and a small fraction of C_{84}) is shown in Fig. 1.

If the energy of the laser is further increased, the intensity of C_{60}^- peak become lower and broader and some other peaks start to appear. This is a sign of C_{60} breakage. These smaller ions are made up of an even number of carbon atoms and have been described earlier in the literature.[6] They are recognizable by its isotopic distribution, although a further laser power increase blurs this fingerprint, making the isotopic distribution to collapse into a single broad peak. Also at a relatively high laser power (70 au) some other carbon clusters are detected. An example of mass spectrum demonstrating the formation of positively charged higher carbon clusters is given in Fig. 2.

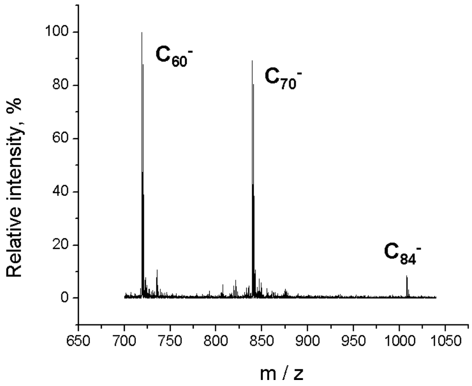

Fig. 1. Negative-ion LDI (linear mode) mass spectrum of a mixture of fullerenes (1 μl of a fullerene mixture 72 ppm in toluene; laser power of 40 au)

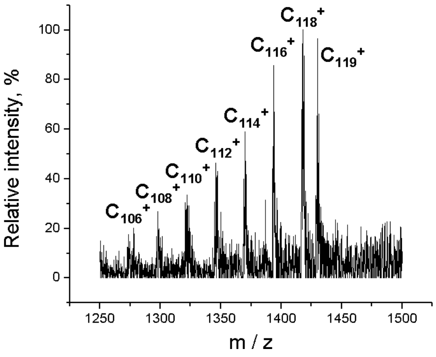

Fig. 2. Formation of other carbon clusters (1 μl of 0.1 mM C_{60}; laser power of 70 au)

LDI and MALDI time-of-flight mass spectrometry of uranium

LDI-TOFMS: In this case laser desorption ionization was applied, i.e., no matrix was used. Positive-ion mass spectra obtained for uranyl nitrate and different laser power measured in LDI linear mode for three different laser energies are shown in Fig. 3. As the energy of the laser increases, the reduction of uranium(VI) goes from UO_2^{2+} (not observed) to U(V) and U(III) species, namely to UO_2^+ and UO^+ ions.

The presence of UO_2^+ ion is observed at a relatively low laser powers (70 au). In comparison with Kratos Kompact MALDI III TOF mass spectrometer,[4] AXIMA TOF mass spectrometer offers a remarkably improved detector. The peak of UO_2^+ ion was observed together with UO^+ and U^+ with the former instrument as a consequency of the necessity to apply higher laser energy which lead to the formation of the ion such as U^+.[4] In Fig. 4, the $^{238}UO_2^+$-peak intensity as a function of the laser power (60–90 au) is shown. As the laser power increases (in the studied interval), so does the intensity. However, the resolution starts to decrease at laser energy >80 au.

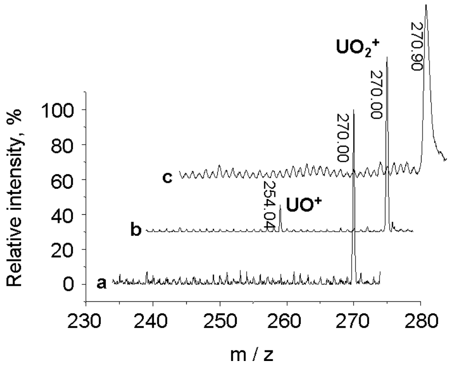

Fig. 3. Positive-ion LDI mass spectra (linear positive) for uranyl nitrate at three different laser powers. a: 70 au; b: 80 au; c: 90 au [1 μl of 0.1 mM $UO_2(NO_3)_2$ aqueous solution]

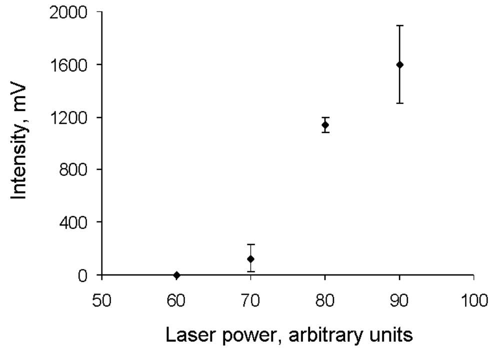

Fig. 4. Intensity of UO_2^+ peak against laser power [1 μl of 0.1 mM $UO_2(NO_3)_2$ aqueous solution] using LDI mode

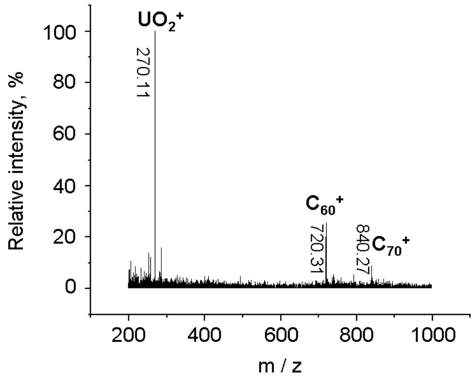

Fig. 5. Simultaneous laser desorption/ionization of uranyl mixture with C_{60} and C_{70} [1 μl of fullerene mixture 72 ppm in toluene followed by 1 μl of 0.1 mM $UO_2(NO_3)_2$ aqueous solution; laser power = 60 au]

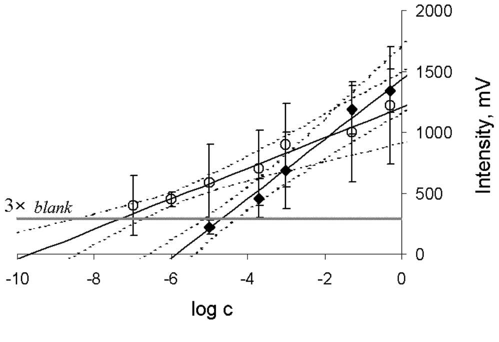

Fig. 6. Determination of uranyl and calibration curves for the determination of uranyl (ionized as UO_2^+) in linear positive mode. Full markers: LDI, empty markers: MALDI using C_{60} as matrix (1 μl of 0.1 mM C_{60} in toluene; laser power of 70 au). Uranium diluted solutions were placed on a target in 1 μl volume

Table 1. Statistical parameters of calibration curves

	LDI	MALDI (C_{60})
β (mV): $b \pm t_{n-2}^{0.05} s_b$	$(2.4\pm0.6)\cdot10^2$	$(1.2\pm0.5)\cdot10^2$
α (mV): $a \pm t_{n-2}^{0.05} s_a$	$(1.4\pm0.3)\cdot10^3$	$(1.2\pm0.3)\cdot10^3$
r^2	0.9896	0.9770
Detection limit (log *c*)	−4.8±0.3	−7.3±0.4

MALDI-TOFMS: The use of C_{60} as a matrix: The use of C_{60} (or a mixture of C_{60} and C_{70}) as a matrix for uranium determination was investigated. Simultaneously, the possible formation of $(C_{60})_x(UO_i)_y$ adducts or endohedral compounds (basically $x = 1, 2, 3$; $y = 1, 2$; $i = 0, 1, 2$; positive or negative ions, mono or doubly charged) was followed. Such species can be easily recognizable in a mass spectrum due to their characteristic isotopic distribution. Especially the 1:1 adduct was of our special interest since endohedral uranium–oxygen fullerenes, $UO_i@C_{60}$ (with UO_i inside the fullerene core) or $U@C_{60}$ have not yet been synthesized. The formation of uranium endohedral complex was observed for C_{82} fullerene, where uranium is encapsulated as $U@C_{82}$.[7–9]

The mixtures of uranyl+C_{60} for different uranyl/fullerene ratios were analyzed, the laser power was varied and linear or reflectron, negative or positive modes were used. In this series of experiments, uranium and fullerenes seems to be ionized independently and no endohedral adducts were observed, just the usual peaks for C_{60}^+, C_{70}^+ and UO_2^+ ions (Fig. 5).

The use of C_{60} as internal standard was examined but it was found that it is not satisfactory because of the relatively high laser power necessary to optimally ionize uranium. This is, however, so high that fullerenes undergo their breakage and thus the ratio of intensities C_{60}/uranium is not stable.

Comparison of calibration curves for the determination of uranium obtained in LDI or MALDI mode using C_{60} as a matrix is shown in Fig. 6. The presence of C_{60} increases the uranium signal but the slope of the calibration curve is lower than that one for LDI.

The equations of the regression line concerning the calibration plots from Fig. 6 are given in Table 1. The procedure of the analysis was the following: 1 μl of aqueous uranyl solution was deposited over a bed of C_{60} previously dried from 1 μl of solution in toluene. After drying in a stream of air at room temperature, the sample was analyzed by MALDI-TOFMS and the results from three measurements were averaged.

MALDI-TOFMS intensity measurements (due to low reproducibility of the sample preparation) are suffering of higher dispersion. That explains rather wide confidence intervals for the estimates of α and β coefficients (a and b) of the regression line:

$$I = \alpha + \beta \log c$$

of the calibration equations. Also the detection limits are determined with rather high errors, such as equal to –4.8±0.3 and –7.3±0.4 for LDI or MALDI, respectively. The presence of C_{60} as matrix enhances the signal of UO_2^+ of two orders of magnitude. Since only 1 μl of the sample is used for the analysis, limit of detection ~50.1 femtomol of uranium is reached with method proposed.

Conclusions

Fullerenes (C_{60} and/or C_{70}) can be easily ionized either to singly charged positive or negative ions. The use of C_{60} (or the mixture of C_{60} and C_{70}) as a matrix increases the sensitivity of uranium determination via UO_2^+ in comparison to LDI mode of ~two orders of magnitude. Detection limits down to $\sim 5 \cdot 10^{-8}$ mol·l^{-1} was reached. The procedure developed can be applied for the determination of uranium traces in waters. The advantage of the method is that very low volume of the sample (1 μl) is needed. Even if the accuracy is not any excellent the method can find use in practice because it enables to analyze a high number of samples in a short time, requires low sampling volume and thus high throughput can be reached.

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