

TRACE ANALYSIS OF URANIUM BY LASER SPECTROSCOPY AND ICP-MS

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Laser spectroscopy

1. Luminescence (TRLIF), Chemiluminescence (TRCH) in **solutions**.

^{238}U LOD - 10^{-13} M, 1ml necessary for analysis or 10^{-16} mole in sample (or $6 \cdot 10^7$ atoms, or $3 \cdot 10^{-10}$ Bq). Determination of **type of molecules** (TRLIF – U VI, TRICH) and **valence state** (TRICH) 10^{-6} M - 10^{-13} M . **Can't determine the isotope composition (1-4)**.

TRICH - The Limits of Detection (LOD) for spectrometers using the registration of chemiluminescence are in the range from 10^{-6} mol/l till 10^{-13} mol/l depending on the type of solutions and type of detectable molecule.

2. Absorption optical spectroscopy. LOD for U-Pu 10^{-4} M – 10^{-5} M. Determination of **type of molecules and valence state**.

3. Laser-Induced Photoacoustic Spectroscopy (LIPAS). LOD - 10^{-6} – 10^{-7} M.

4. Thermal Lens Spectroscopy (TLS). LOD – 10^{-6} – 10^{-7} M.

5. RIMS (**atomic beam**).

LOD 10^5 atoms or less in some cases, **isotope composition determination**.

6. Instrumental Neutron Activation analysis (INAA) depending on cross section and neutron flux. At thermal neutron flux of $\sim 10^{13}$ ($\text{cm}^{-2}\text{s}^{-1}$), LOD - 10^{-5} - $10^{-10}\%$.

Pu, Np, U. M = mole/litre.

$$10^{-13}\text{M} \approx 2.4 \times 10^{-14} \text{g/ml} \approx 6 \times 10^7 \text{atoms/ml}$$

$$10^{-13}\text{M} \quad {}^{239}\text{Pu} = 5.4 \times 10^{-5} \text{Bq/ml};$$

$${}^{238}\text{U} = 3 \times 10^{-10} \text{Bq/ml}; \quad {}^{235}\text{U} = 1.9 \times 10^{-9} \text{Bq/ml};$$

$${}^{237}\text{Np} = 6.2 \times 10^{-7} \text{Bq/ml}$$

Inductively Coupled Plasma (ICP)

ICP-AES, LOD 10ng/ml Pu

ICP-MS LOD 3×10^6 Pu atoms

DF-ICP-MS 40 pg/l ^{235}U , 1.2 pg/l ^{239}Pu ,

^{241}Am (3×10^6 atoms/ml)

ICP-QMS 60 ng/l Np.

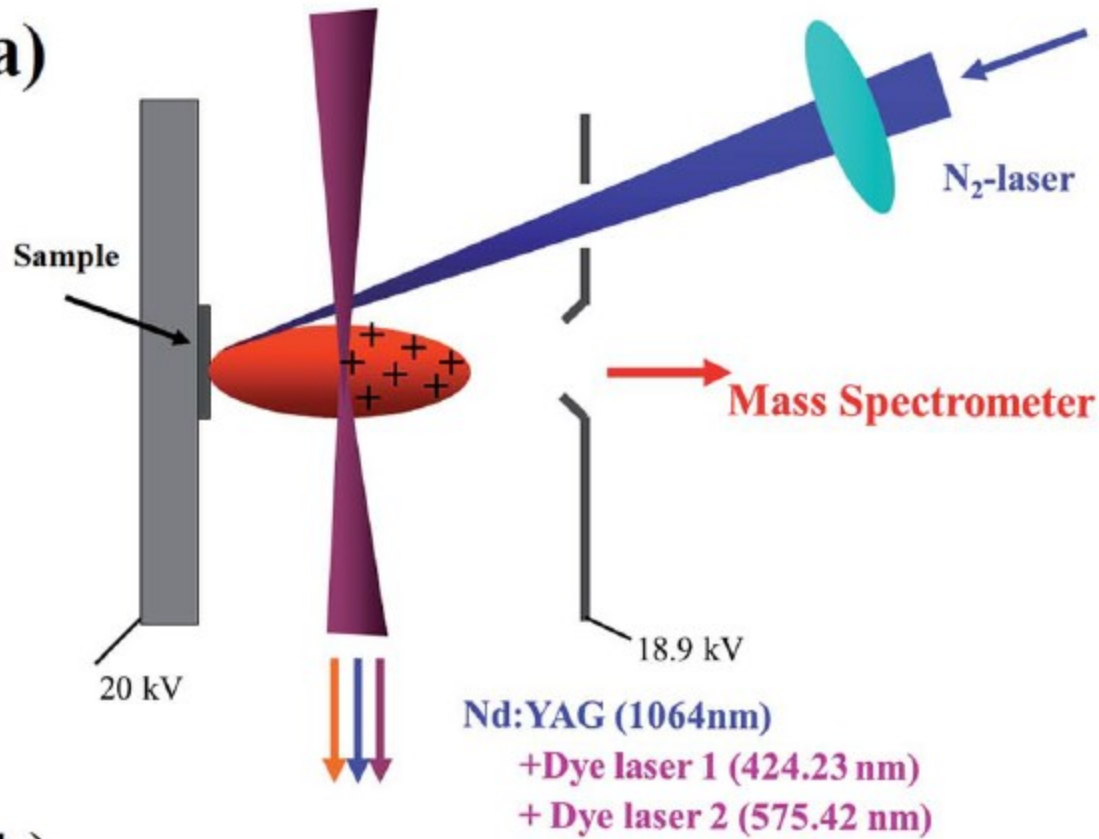
Global Level

Pu – global level i.e. nuclear weapon tests in the 1950-1960s. Up to 10^9 atoms/g of Pu in soil or up to 10^{-3} Bq/g or up to 4×10^{-13} g/g.

LOD DF-ICP-MS for Soil samples 1.3×10^{-13} g/g (^{240}Pu).

One of the most commonly used methods for determining $^{240,239}\text{Pu}$, ^{238}Pu , $^{234,235}\text{U}$, ^{238}U , ^{241}Am in environmental samples relative to the global level is alpha spectroscopy in combination with radiochemical separation. Analysis of a sample containing 10^8 nuclei of ^{239}Pu requires no less than a day of measurements.

a)



b)

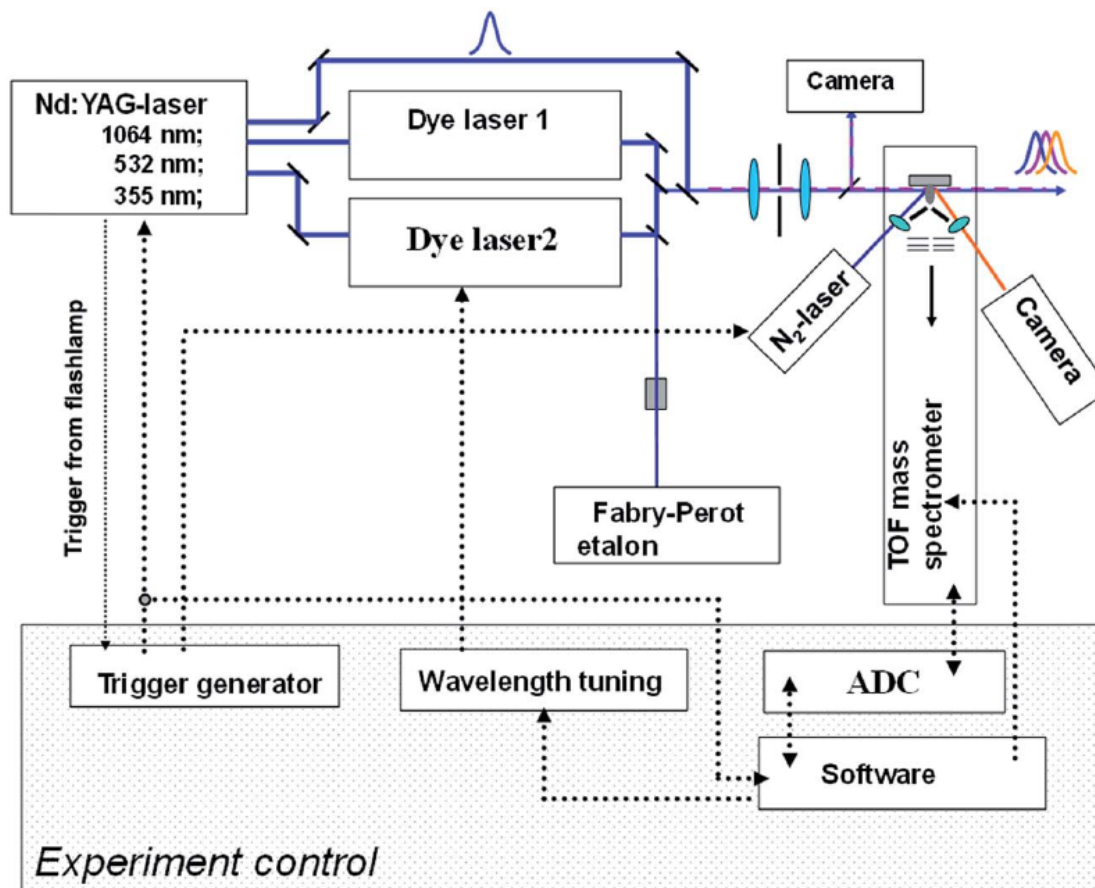


Fig. 1 Diagram of the setup for the detection of uranium isotope ratios by photoionisation mass spectrometry. The samples (solutions or solids) are placed onto a substrate from where they are desorbed with a 337 nm nitrogen laser. The neutral species are resonantly ionised by a set of tunable dye lasers pumped by a Nd:YAG laser (355 nm and 532 nm) beam. Part of the fundamental 1064 nm Nd:YAG laser beam is also used for ionisation. The photoions are detected by a TOF-mass spectrometer in linear or reflectron modes. The delay between the desorption and photoionisation pulses of ~ 600 ns is generated by a trigger generator which in turn is triggered by a pulse from the flash lamp of the Nd:YAG laser.

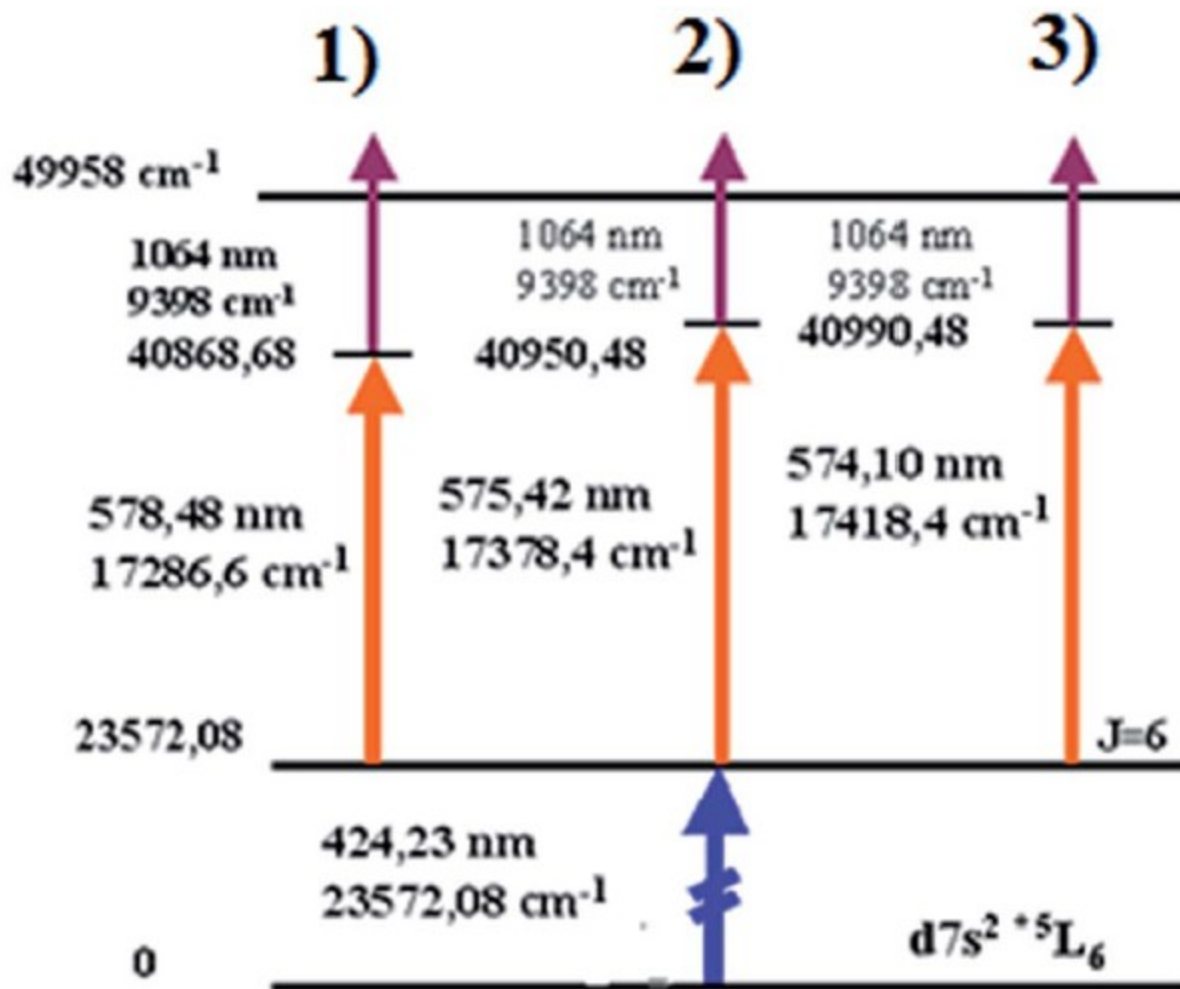


Fig. 6 Most efficient uranium photoionisation schemes. The first UV transition dye laser works on Stilbene 3 ($\sim 1 \mu\text{J}$ per pulse) followed by the second transition excited by the dye laser on Rhodamine 6G ($\sim 20 \mu\text{J}$ per pulse). A part of the fundamental 1064 nm radiation from the Nd:YAG laser ($\sim 1 \text{ mJ}$ per pulse) ionises atoms into the continuum.

Table 1 Isotope ratios of reference uranium standards having different $^{235,238}\text{U}$ isotope compositions detected by the photoionisation mass spectrometry method. Total uranium content of the samples is 5×10^{13} atoms

| | $^{235}\text{U}/^{238}\text{U}$ reference standard value ²⁹ | $^{235}\text{U}/^{238}\text{U}$ photoionization method |
|---|--|--|
| 1 | 0.047326(35) | 0.0492(20) |
| 2 | 0.030786(22) | 0.0328(13) |
| 3 | 0.020062(15) | 0.02101(11) |
| 4 | 0.0072617(51) | 0.00715(54) |
| 5 | 0.0032169(20) | 0.00332(36) |

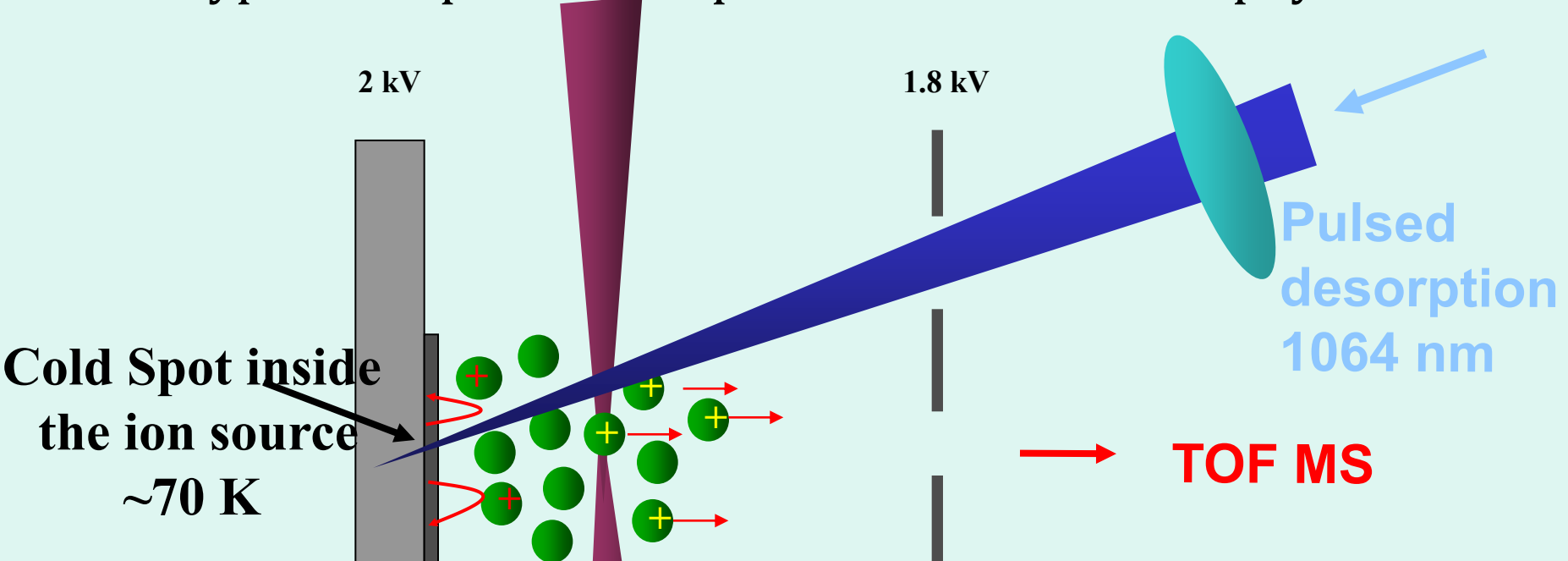
$\sim 1 : 1$ uranium solution is presented. The measurement results of the 5 reference samples with isotope ratios varying from depleted ($^{235}\text{U}/^{238}\text{U} = 0.0032$) to slightly enriched uranium ($^{235}\text{U}/^{238}\text{U} = 0.047$) are presented in Table 1. The errors, that are 2σ errors, are calculated from 10 repeat measurements and do not exceed 7%.

Table 2 Isotope ratios of natural uranium detected with the photoionisation mass spectrometry method. A sub-fg detection limit (^{235}U) has been determined using uranium methanol solutions having concentrations varying by several orders of magnitude. At these low level concentrations the measurement of meaningful isotope ratios is still possible with the precision of <7% (2σ errors)

| | Total U content, atoms per sample | Amount of desorbed U, atoms per laser area | ^{235}U content, g per sample | ^{238}U content, g per sample | Experimental ratios, $^{235}\text{U}/^{238}\text{U}$ |
|---|--------------------------------------|---|---|---|---|
| 1 | 5×10^8 | 10^6 | 6×10^{-18} | 8.24×10^{-16} | Qualitative analysis |
| 2 | 5×10^9 | 10^7 | 6×10^{-17} | 8.24×10^{-15} | Qualitative analysis |
| 3 | 5×10^{10} | 10^8 | 6×10^{-16} | 8.24×10^{-14} | 0.00752(91) |
| 4 | 5×10^{11} | 10^9 | 6×10^{-15} | 8.24×10^{-13} | 0.00731 (68) |
| 5 | 5×10^{13} | 10^{11} | 6×10^{-13} | 8.24×10^{-11} | 0.00702 (57) |
| 6 | 5×10^{15} | 10^{13} | 6×10^{-11} | 8.24×10^{-9} | 0.00692 (41) |
| 7 | 5×10^{16} | 10^{14} | 6×10^{-10} | 8.24×10^{-8} | 0.00718 (30) |

tion).³⁴ The measurement results are presented in Table 2. The isotope ratios were determined with errors not exceeding 10% (2σ errors) for uranium concentrations down to 5×10^{10} atoms per sample (or ~ 80 fg per sample). Below this level only a qualitative analysis is possible, mainly due to the data

Laser Resonance Photoionisation Mass Spectrometry- Krypton isotopes for non proliferation and astrophysics.



~1% precision for 10^6 total Kr atoms, reproducible to the same level within a week.
Sensitivity < 1000 atoms.

Nd:YAG
(+Tunable Dye Lasers)



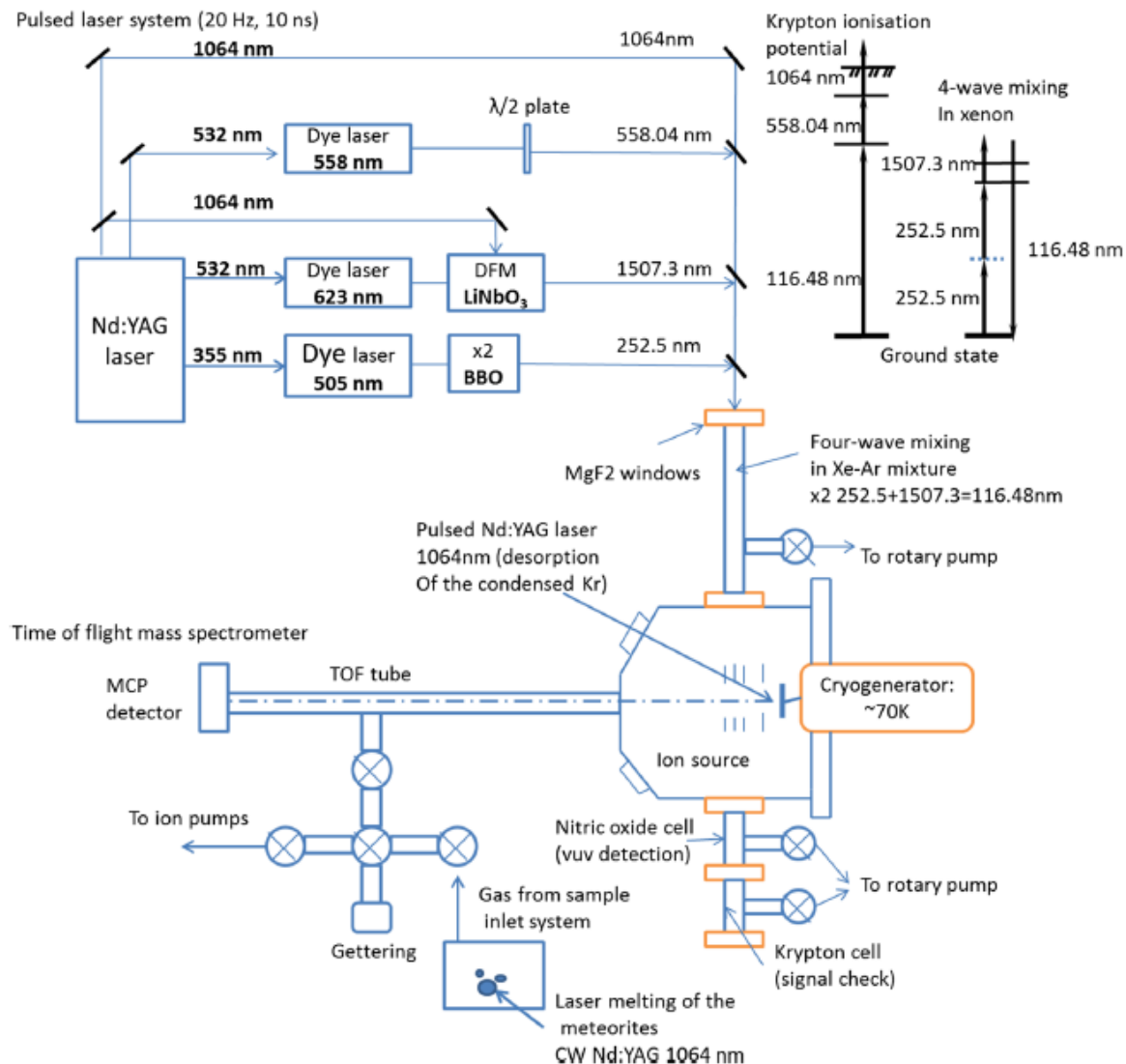
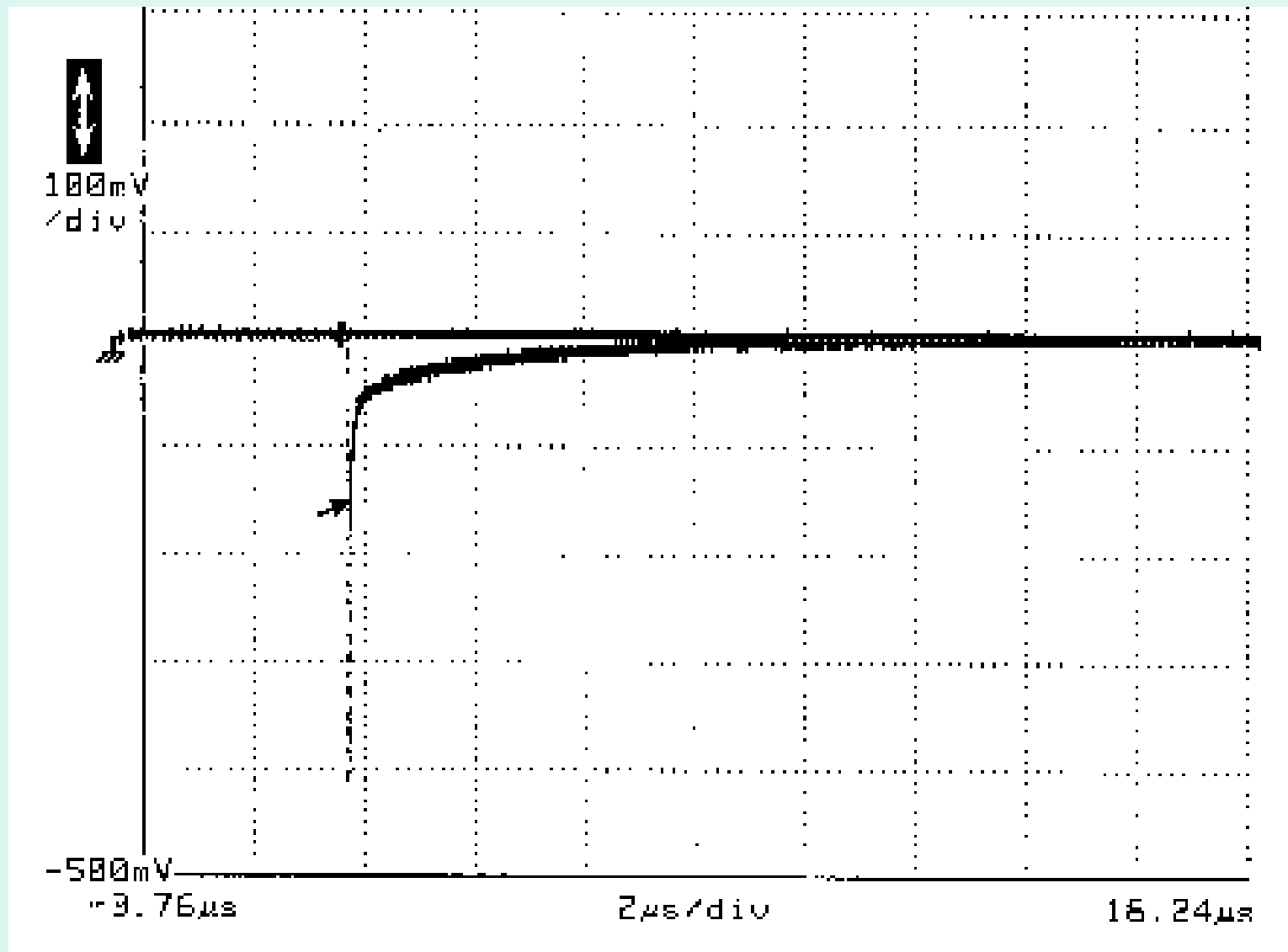
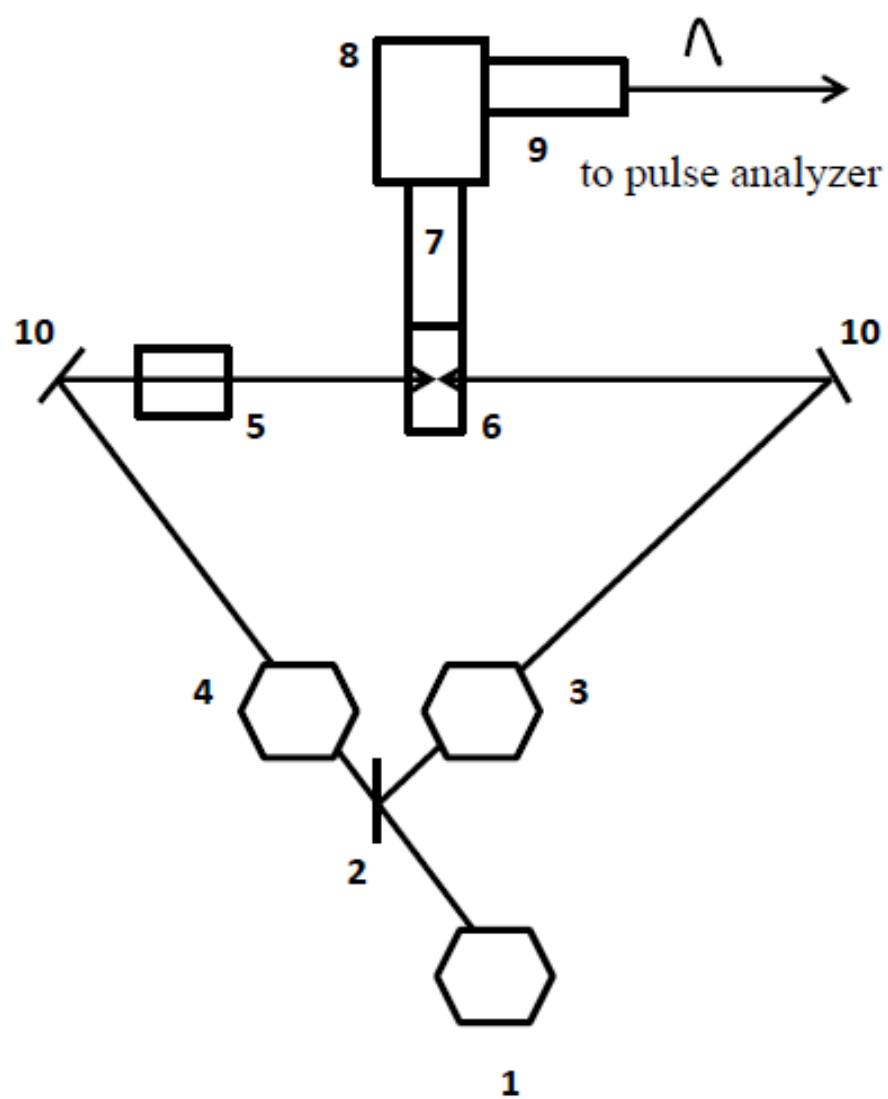


Fig.1 Schematic of the Resonance Ionisation Mass Spectrometer for ultra-trace detection of Krypton Isotopes (RIMSKI). The solids (meteorites/small grains) are step-heated by a 1064 nm CW Nd:YAG laser and the krypton atoms diffused out of the sample are introduced into the ion source of the time of flight mass spectrometer. The atoms then are condensed onto the cold substrate (70 K) placed behind the

extraction electrode of the ion optics. The pulsed 1064 nm Nd:YAG laser beam evaporates the condensed atoms from the substrate, and the atoms are resonantly excited from the ground state into ionisation continuum by a set of pulsed ns dye lasers. The resonance ionisation scheme involves a vacuum ultraviolet 116.4 nm transition followed by 558.04 nm and 1064 nm

TRLIF allows to decrease considerably the background from laser pulse. and has a sensitivity up to 10^{-13} mol/l



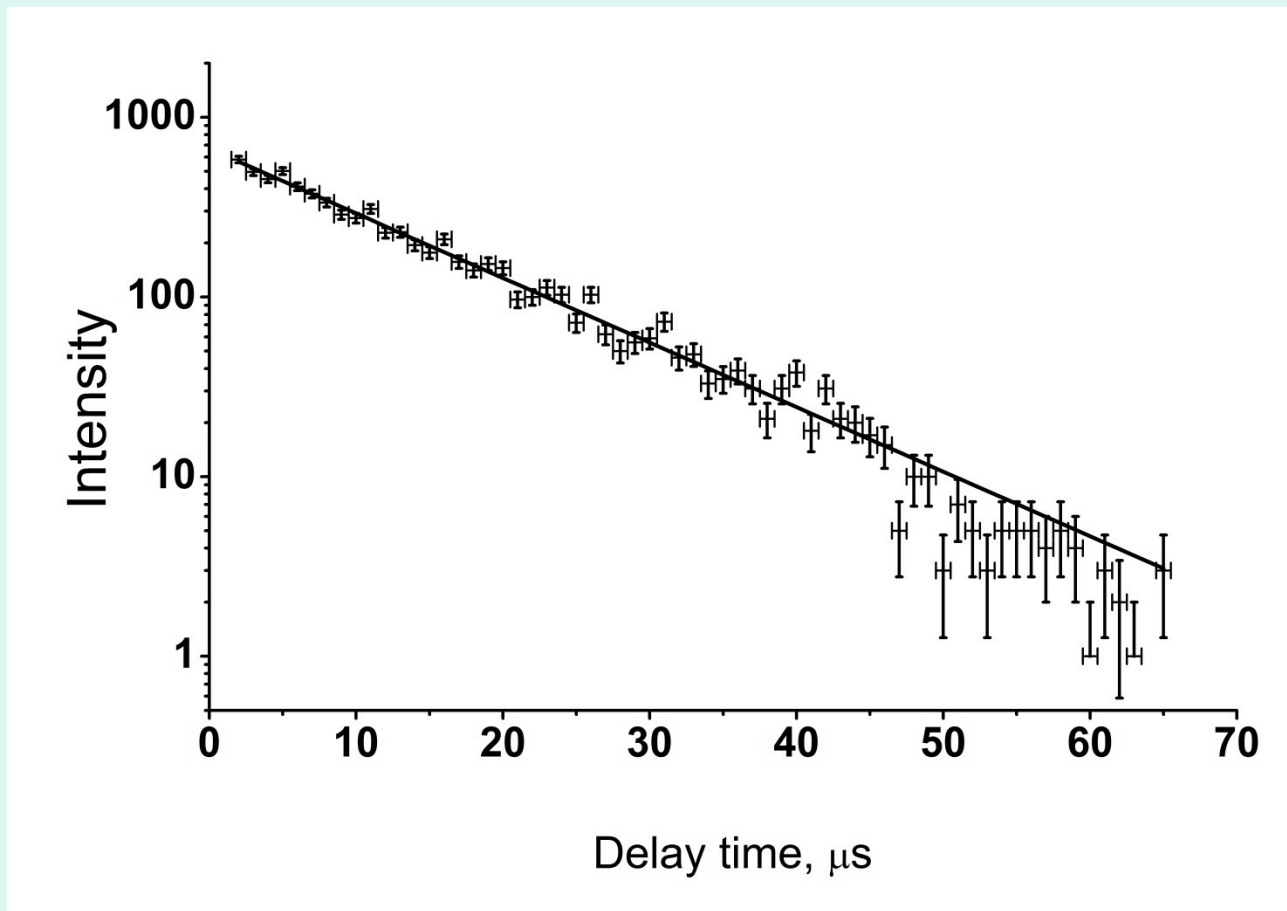


(1) nitrogen laser OBB-1010, (2) beam splitter, (3) dye laser OBB-1011, (4) dye laser OBB-1012, (5) optical delay line OPD-1, (6) cuvette with solution, (7) optical fiber, (8) monochromator DMR-4, (9) photomultiplier, (10) mirror



Experimental set-up for chemiluminescence spectroscopy of actinides in aqueous solutions





Photoluminescence of $\text{UO}_2\text{F}_5^{3-}$ in $\{\text{H}_2\text{O} + \text{CsF}[42\%]\}$ solution. pH=9.0. Excitation by nitrogen pulse (10 ns) laser. Registration at $\lambda=520$ nm, $\delta\lambda=9$ nm. Gate time 1 μs . 200 laser pulses per channel were made. Laser beam diameter 5 mm, power in laser pulse 15 kW. Luminescence lifetime $\tau = 12.08 \pm 0.25$ μs

TRLIF – *time resolved laser induced fluorescence*

pulse laser ($\sim 10^{-8}$ s) for excitation and luminescence registration after delay ($\sim 10^{-6}$ s).

Eu⁺³, Tb⁺³, Gd⁺³, Dy⁺³, Sm⁺³, Ce⁺³, Tm⁺³ lanthanides and UO²⁺, Cm³⁺, Am³⁺, Cf³⁺, Es³⁺, Bk³⁺ actinides ions give direct luminescence in solutions and may be detected by TRLIF method

Limit of lanthanides detection (LOD) by TRLIF method in mol/l (M)

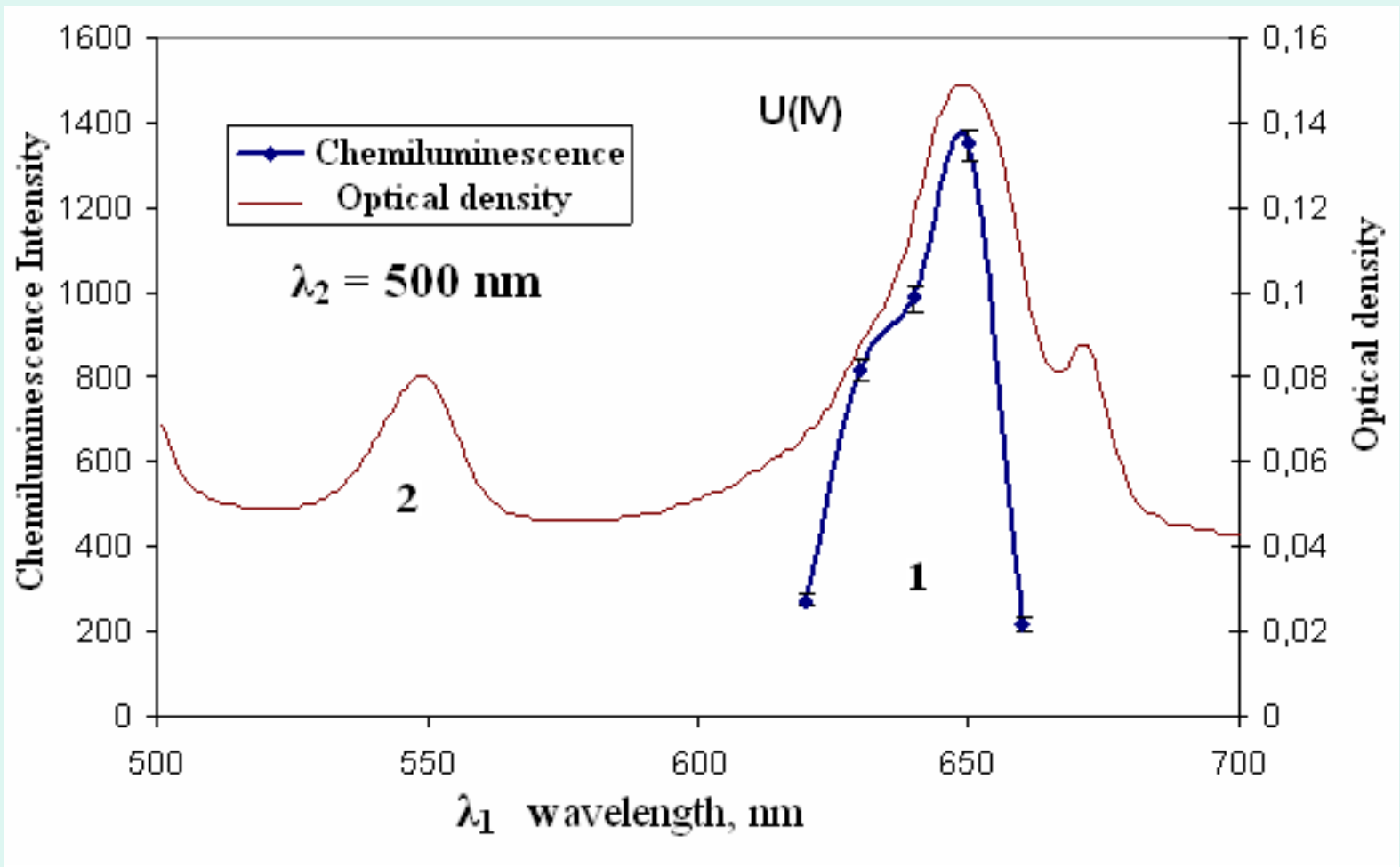
| Element | Eu ³⁺ | Tb ³⁺ | Gd ³⁺ | Dy ³⁺ | Sm ³⁺ | Ce ³⁺ | Tm ³⁺ |
|----------|-------------------|------------------|------------------|-------------------|-------------------|------------------|------------------|
| LOD in M | 10 ⁻¹² | 10 ⁻⁹ | 10 ⁻⁸ | 10 ⁻¹⁰ | 10 ⁻¹⁰ | 10 ⁻⁹ | 10 ⁻⁶ |

Limit of actinides detection (LOD) by TRLIF in mol/l (M)

| Element | UO ²⁺ | Cm ³⁺ | Am ³⁺ |
|---------|---------------------|---------------------|--------------------|
| LOD | 10 ⁻¹³ M | 10 ⁻¹³ M | 10 ⁻⁹ M |

No direct luminescence from Np, Pu in solutions. We have observed the chemiluminescence in solutions induced by the actinides complexes (Pu, Np, U) excited by the pulse laser radiation with delay time after laser pulse.

The TR chemiluminescence technique may be used for **non-luminescent** actinides (Pu and Np) and **non-luminescent** molecules containing U, Pu, Np detection.



1. Luminol+U(IV)+HCl. Chemiluminescence intensity dependence on the wavelength of laser radiation at the first excitation step. When the wavelength of laser radiation corresponds to the wavelength of U(IV) absorption band than the intensity of luminal chemiluminescence is increased. The wavelength of laser radiation at the second step was fixed at 500 nm (two steps-two colors scheme).
2. Absorption spectrum of U(IV)+HCl solution.

Some Mass Spectrometers available in our labs. (See the full list of Manchester equipment:

<http://www.chemistry.manchester.ac.uk/our-research/facilities>



Thermo Orbitrap LCMS –high res. ES, APCI, APPI, ASAP



Waters, SQD2 quadrupole LCMS



Agilent Quadrupole LCMS



Bruker QTOF MS/MS
Accurate mass, ESI



Agilent GCMS, EI

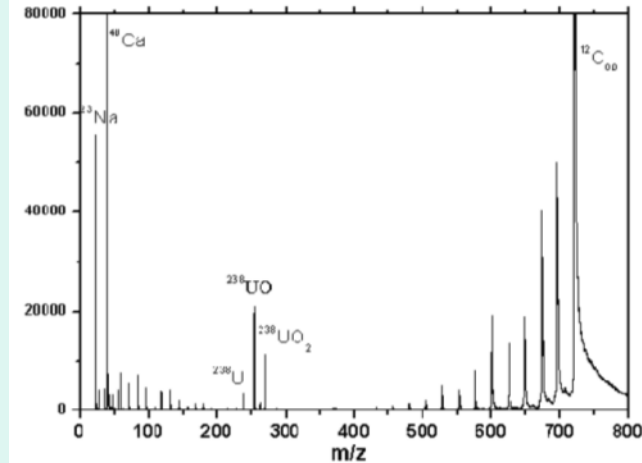


Bruker ETP, MS/MS, ESI

MALDI - TOF mass spectrometry: analysis of particles



Nitrogen 337 nm laser

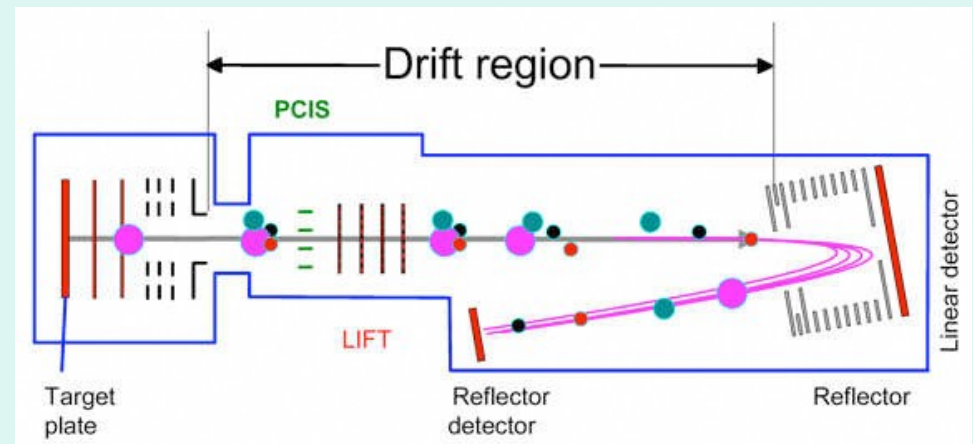


MALDI sample plate – samples dry on a plate and later ionised with 337 nm laser.

Natural uranium (<1 ppm) in kaolinite mineral. Fullerene matrix is used for enhancement of the signal.



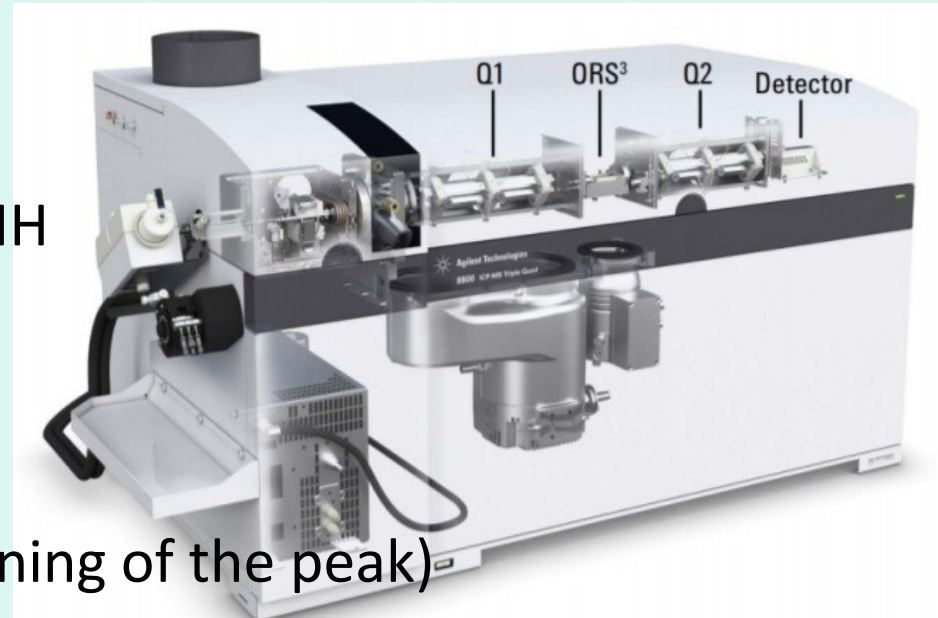
Schmatzu MALDI TOF mass spectrometer



Matrix Assisted Laser Desorption Ionisation Mass spectrometry (MALDI) – mixing (usually biomolecules of very high masses with Organic matrix allowing soft ionisation reducing or completely eliminate their fragmentation.

Trace analysis ICPMS/ LA ICPMS (ppb detection/
high dynamic range, sometimes (with old
equipment) problems with isobaric interferences.
Practically solved in the new Agilent 8900 ICPMS
system.

$^{129}\text{I}/^{127}\text{I}$ of 10^{-7} in NIST 3231 SRM
Problem of tailing from ^{127}I and ^{127}IH
 ^{90}Sr : spectral overlap from ^{90}Zr ;
 ^{137}Cs : spectral overlap with ^{137}Ba
 ^{236}U : isobars at $^{235}\text{UH}^+$
 ^{237}Np in presence of ^{238}U (broadening of the peak)



Agilent 8900 MS/MS system

Minor problems, including sample prep., however precision and
detection limits are excellent as *sub-ppb* (stability too!)

Analysis of archaeological samples



- Prehistoric bones of dinosaur and southern mammoths, ancient bones of bear and archantrope as well as the samples of surrounding soils; everything collected in different parts of Uzbekistan.
- Dissolution of the samples in nitric acid
- NIST certified standards
- Both INAA (Tashkent) and ICP-MS (Manchester) methods used
- 64 elements analysed

Ivory and jaw bones of the Southern Mammoth

CONCLUSION

1. The resonance ionization spectroscopy in combination with mass spectrometry (**RIMS**) has been successfully used for the development of the state of the art instruments capable of detection of isotope ratios at *fg*-level.
2. Luminescence (TRLIF) and Chemiluminescence (TRLIC):
LOD up to 10^{-9} - 10^{-13} mol/l, 1ml need for analysis.
3. We have applied ICP-MS method and analysed the elemental composition (**64 elements**) of bones of dinosaurs, South mammoths, prehistoric bear and archanthropus as well as the samples of surrounding soils; everything collected in different parts of Uzbekistan. South mammoth (220mg/kg), prehistoric bear (24mg/kg) and archanthropus (1.5mg/kg) compared to surrounding soils (3.7-7.8 mg/kg) and standard bones (<0.01mg/kg) was established. The standard ratio $^{235}\text{U}/^{238}\text{U} = 0.007$ was detected for all samples, but the $^{234}\text{U}/^{238}\text{U}$ (detected 1.6×10^{-4} - 5.8×10^{-5}) ratio sometimes differ from secular equilibrium value (secular equilibrium $^{234}\text{U}/^{238}\text{U} = 5.5 \times 10^{-5}$).

We invite Colleagues to work together to analyze the data obtained and search for interesting samples for analysis