

SAMPLE ANALYSIS BY LASER SPECTROSCOPY, ICP-MS, RIMS AND INAA

I.N. Izosimov, JINR, Dubna, Russia

I. Strashnov, The University of Manchester,
United Kingdom

B.D. Saidullaev, A. Vasidov, Nuclear Physics Institute,
Uzbekistan

- Today the laser spectroscopy methods applied for trace analysis may be classified as methods
 - for isotope composition determination (RIS, RIMS) and
 - methods for type of elements and valence states determination (TRLIF, TRLIC).

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.

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 $10^{-4}\text{M} - 10^{-5}\text{M}$. 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.

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

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

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

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

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.

Pu Global Level in different Objects.

Pulmonary tissue – $(1-50) \times 10^{-6} \text{Bq/g}$;

Lymph nodes – $(2-360) \times 10^{-6} \text{Bq/g}$;

Liver – $(0.5-80) \times 10^{-6} \text{Bq/g}$;

Bony tissue – $(1-40) \times 10^{-6} \text{Bq/g}$;

Soils – up to 10^{-3}Bq/g ;

Seawater – up to $10^{-5} - 10^{-6} \text{Bq/l}$.

^{238}U (99.283%) + ^{235}U (0.711%) + ^{234}U (0.0054) – $2.5 \cdot 10^4$ Bq/g natural uranium.

^{238}U - $1.25 \cdot 10^4$ Bq/g.

^{234}U - member of ^{238}U decay chain

natural radioactivity N : $^{238}\text{U} \approx ^{234}\text{U} \approx 21x^{235}\text{U}$ or $N \approx 2 \cdot ^{238}\text{U}$ Bq.

U in:

Soils - $3 \cdot 10^{-6}$ – $5.1 \cdot 10^{-4}$ %;

Seawater – 3 ng/ml;

Blood - $4 \cdot 10^{-10}$ g/g;

Urine - 0.04-5 ng/ml;

Kidneys – $1.3 \cdot 10^{-8}$ g/g – $5.3 \cdot 10^{-9}$ g/g;

Liver - $6 \cdot 10^{-9}$ g/g;

Heart - 10^{-10} g/g;

Brain - 10^{-10} g/g;

Lung - $6 \cdot 10^{-9}$ — $9 \cdot 10^{-9}$ g/g;

Bony tissue – 10^{-9} g/g;

Hair – $1.3 \cdot 10^{-7}$ g/g.

Typical concentration of uranium
in blood plasma is about 0.05ng/ml – 0.5ng/ml,
in urine is about 0.2ng·ml⁻¹ – 5ng·ml⁻¹.

Compare in different time concentrations of the
uranyl in blood plasma and in urine one can
estimate the time when the uranyl was got into
organism.

- Sensitive and direct detection of the trace amounts of actinide detection and **simultaneously determination of the actinides oxidation states and type of molecules containing actinides** present today major importance for ecology, radwaste handling and control, rehabilitation of contaminated areas and risk assessment.
- Luminescence spectroscopy is very attractive, because its **theoretical** sensitivity is limited **in principle** only by intensity of excitation beam.

Practical use:

it is necessary to get the investigated element (isotope) from the sample to the zone of interaction with laser radiation and have such element (isotope) in this zone for a long time.



From the practical point of view beneficial to use the solutions of investigated samples (TRLIF, TRLIC).

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 UO^{2+} , Cm^{3+} , Am^{3+} , Cf^{3+} , Es^{3+} , Bk^{3+} 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}

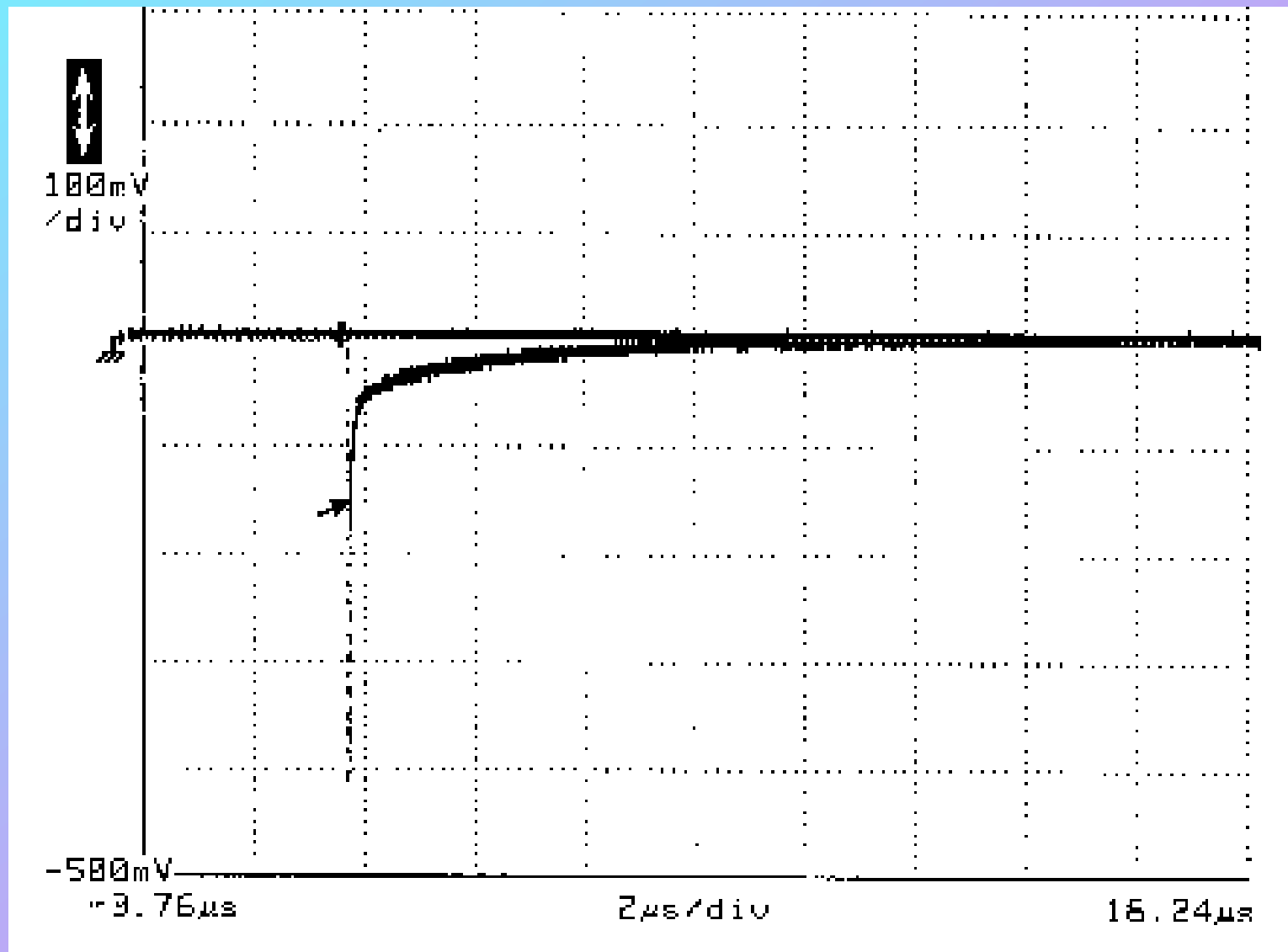
Limit of actinides detection (LOD) by TRLIF in mol/l (M)

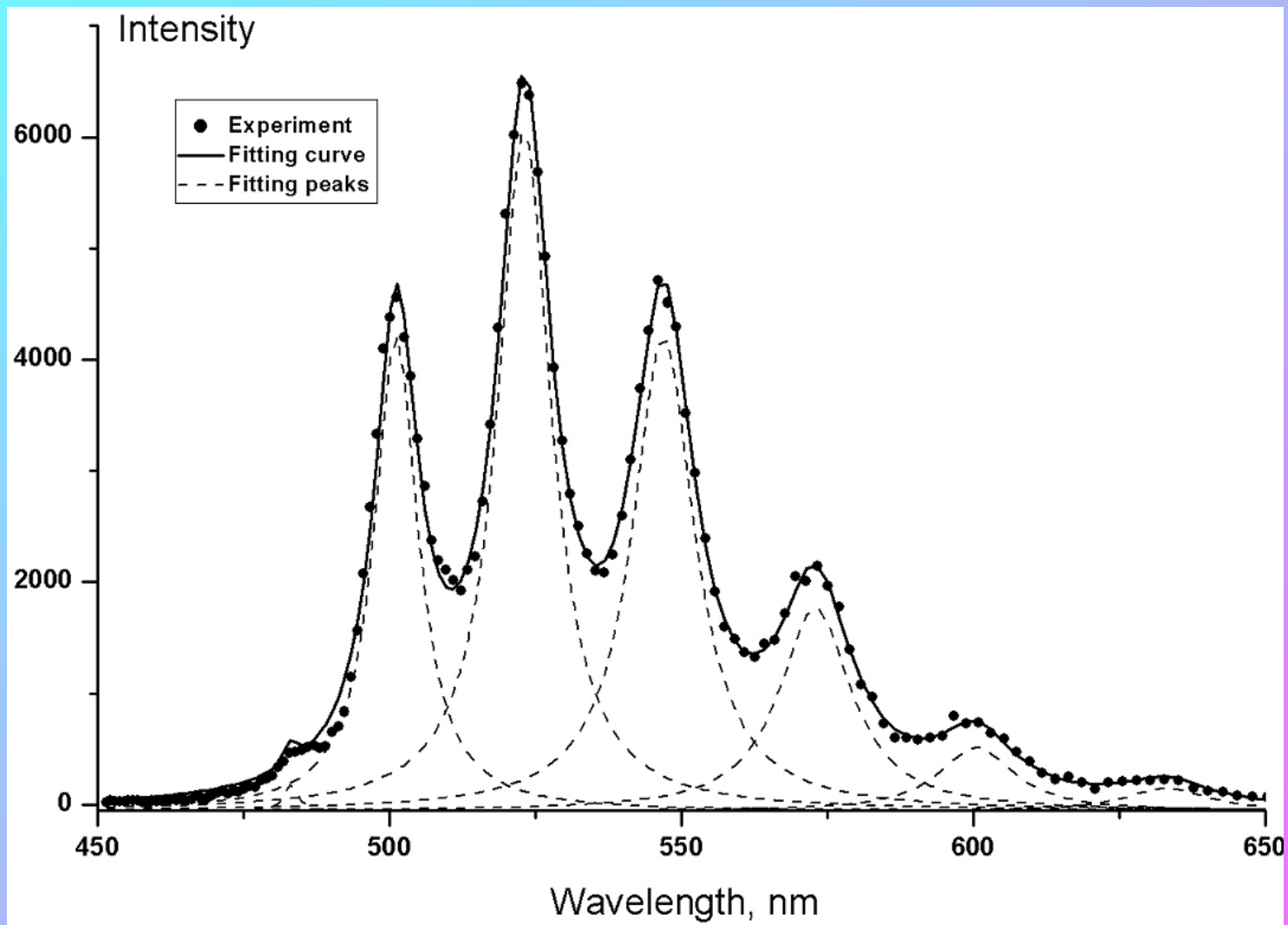
Element	UO^{2+}	Cm^{3+}	Am^{3+}
LOD	$10^{-13}M$	$10^{-13}M$	$10^{-9}M$

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.

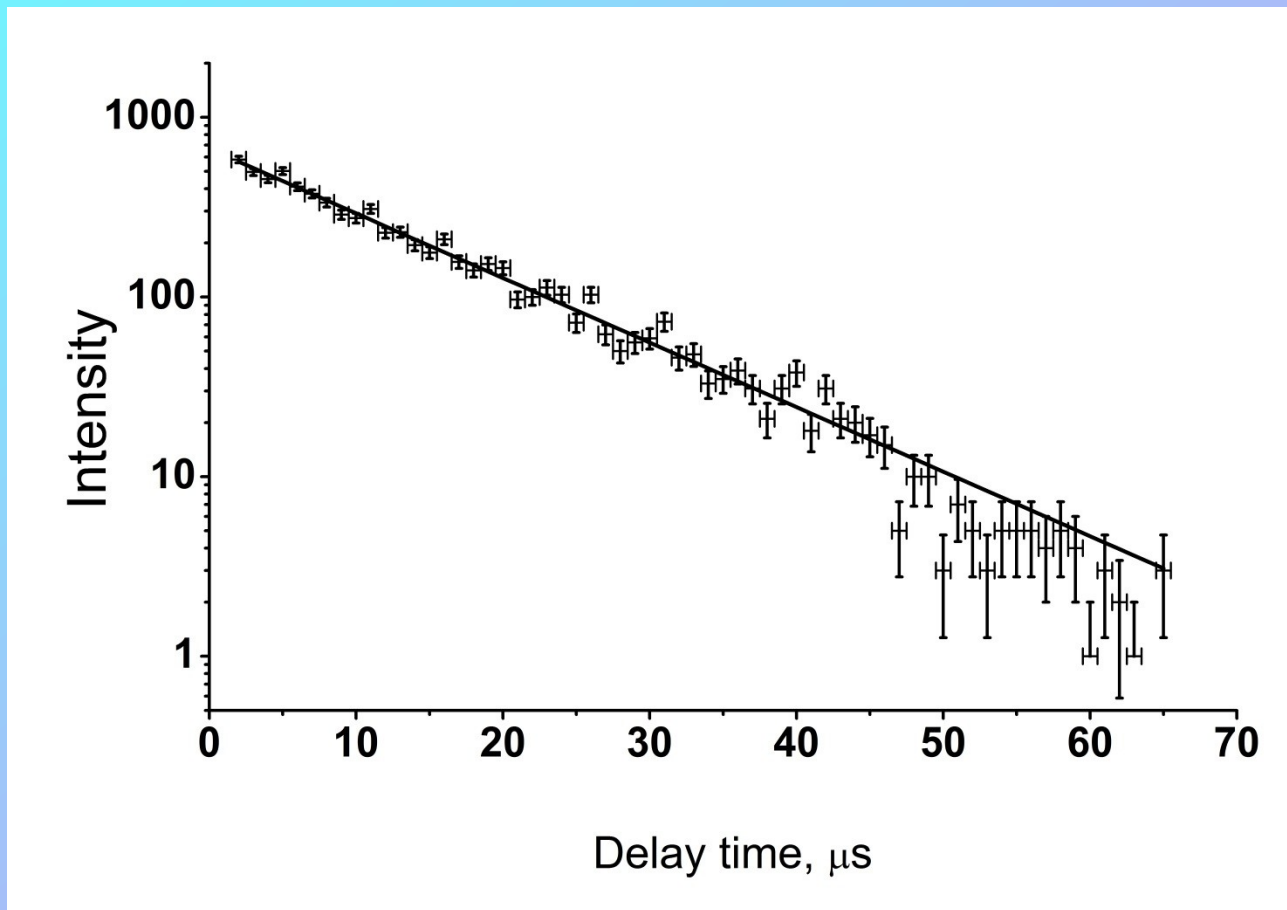
The TR chemiluminescence technique may be used for **non-luminescent** actinides (Pu and Np) and **non-luminescent** molecules containing U, Pu, Np detection.

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

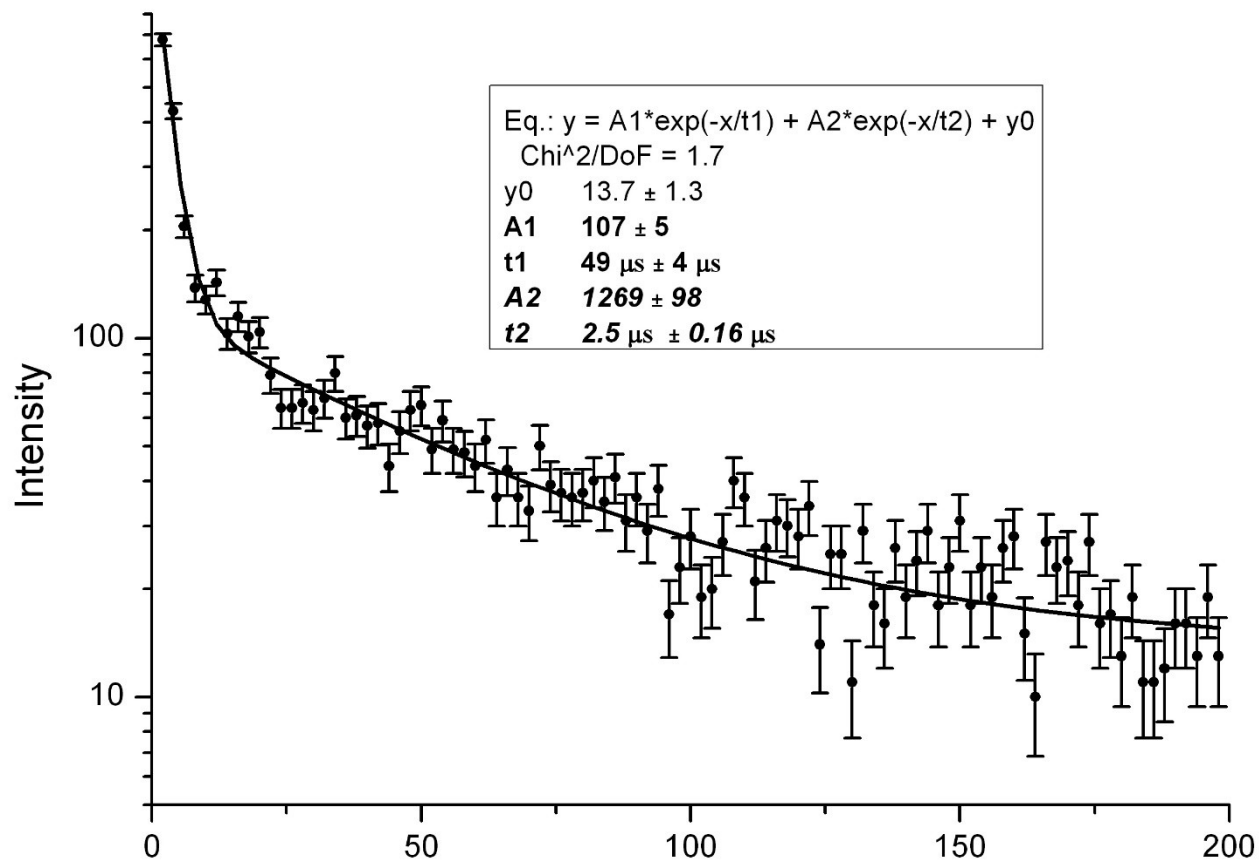




Separation of peaks in the luminescence spectrum of uranyl



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



Time, μs. Luminescence of the Dy in K₂CO₃ solution

Excitation by pulse (10ns) nitrogen pulse laser, registration wavelength 480nm,
gate time 2μs.

Biological samples containing a large amount of organic substances should be preliminary mineralized.

Typical concentration of uranium

in blood plasma is about $0.05\text{ng}\cdot\text{ml}^{-1}$ – $0.5\text{ng}\cdot\text{ml}^{-1}$,

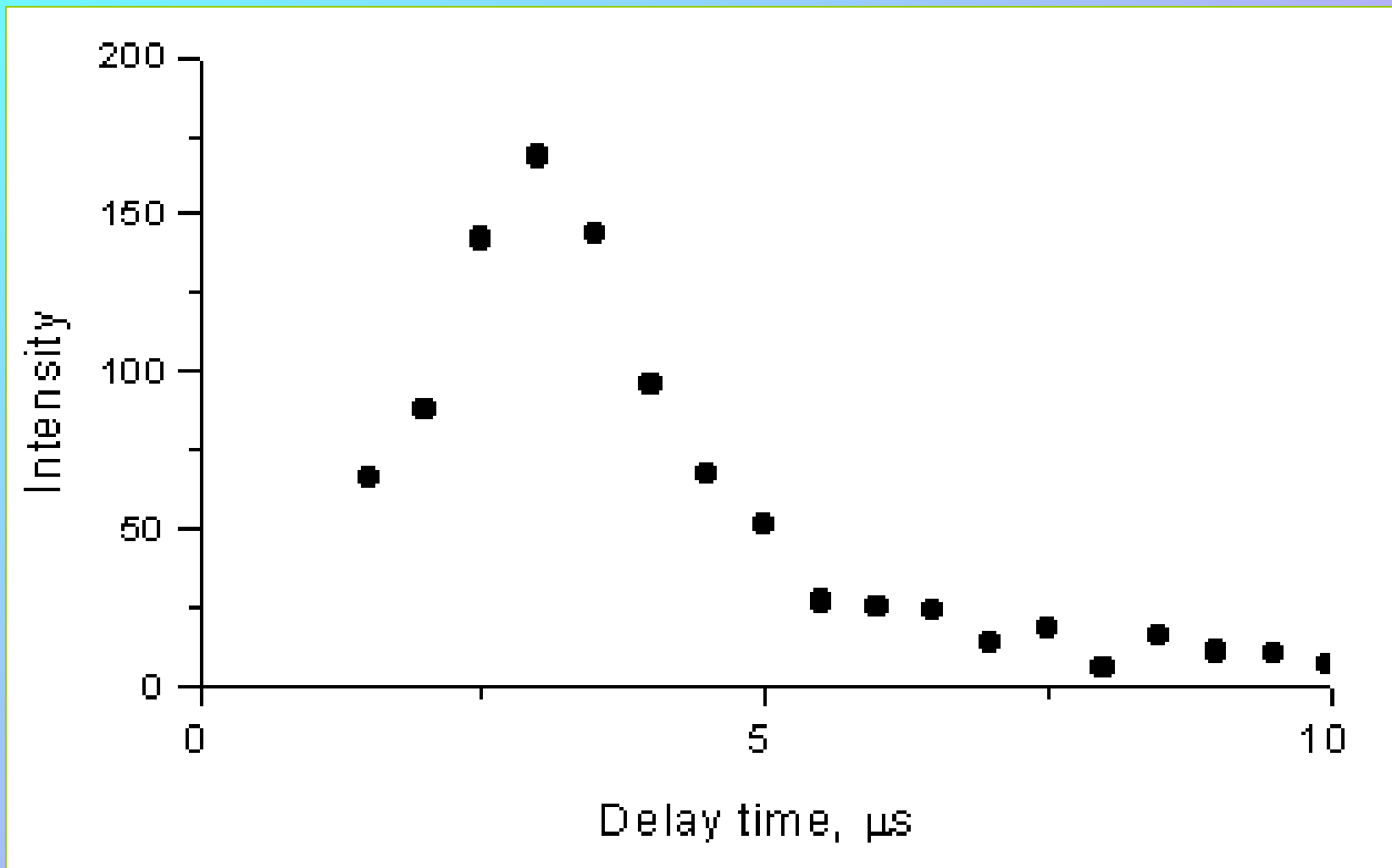
in urine is about $0.2\text{ng}\cdot\text{ml}^{-1}$ - $5\text{ng}\cdot\text{ml}^{-1}$.

Without mineralization the limit of uranyl detection in blood plasma was $0.1\text{ ng}\cdot\text{ml}^{-1}$.

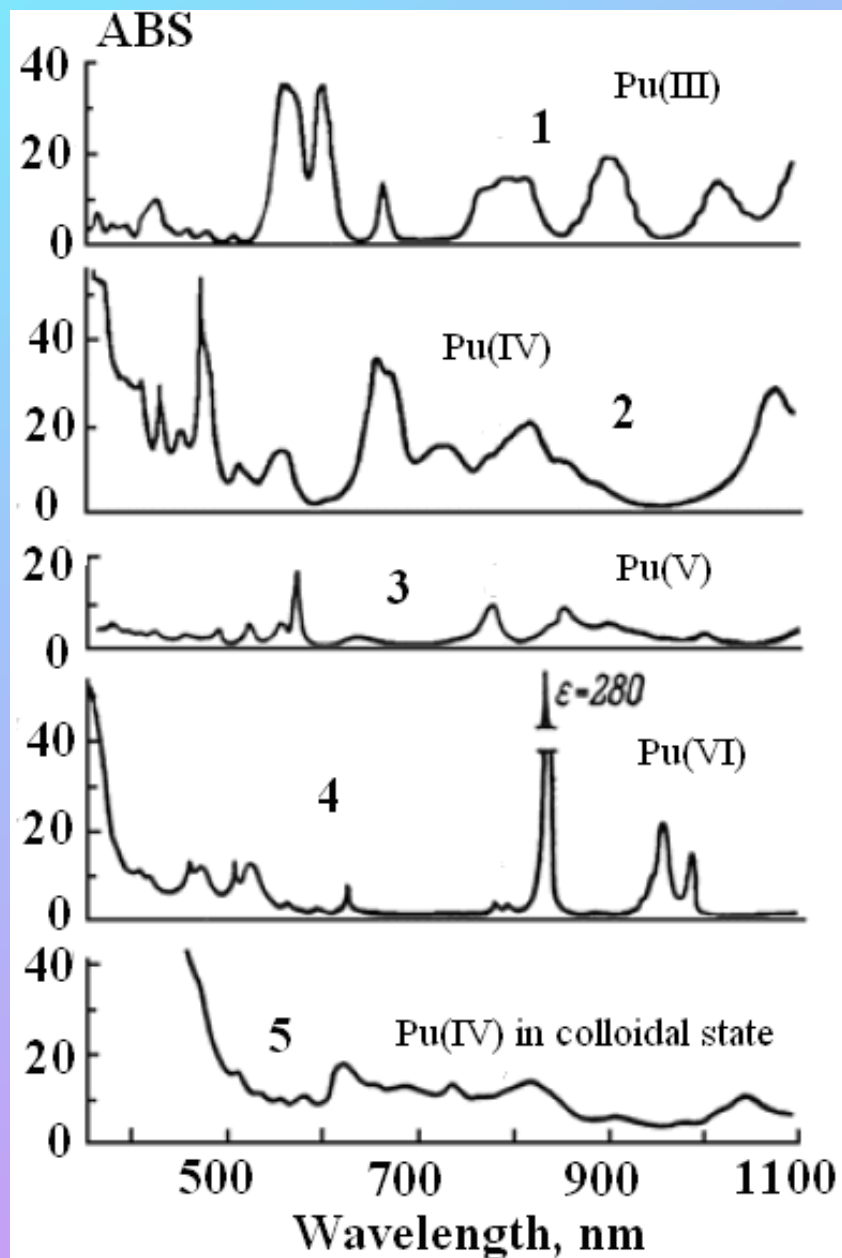
After mineralization was up to $0.008\text{ ng}\cdot\text{ml}^{-1}$ - $0.01\text{ ng}\cdot\text{ml}^{-1}$.

The limit of uranyl detection in urine in our TRLIF experiments was up to $0.005\text{ ng}\cdot\text{ml}^{-1}$.

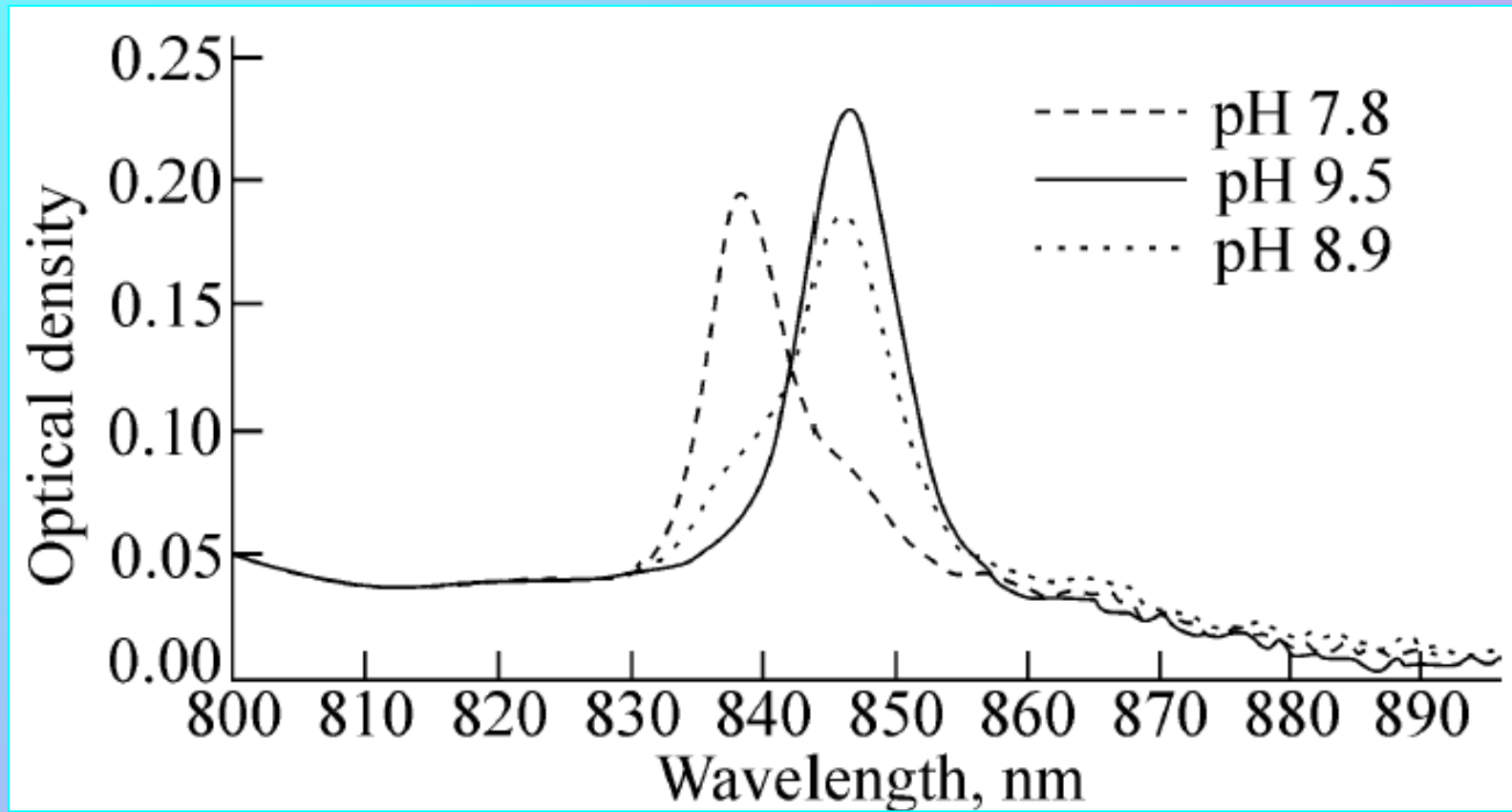
limit of detection of europium was $0.015\text{ ng}\cdot\text{ml}^{-1}$ and samarium, $0.2\text{ ng}\cdot\text{ml}^{-1}$.



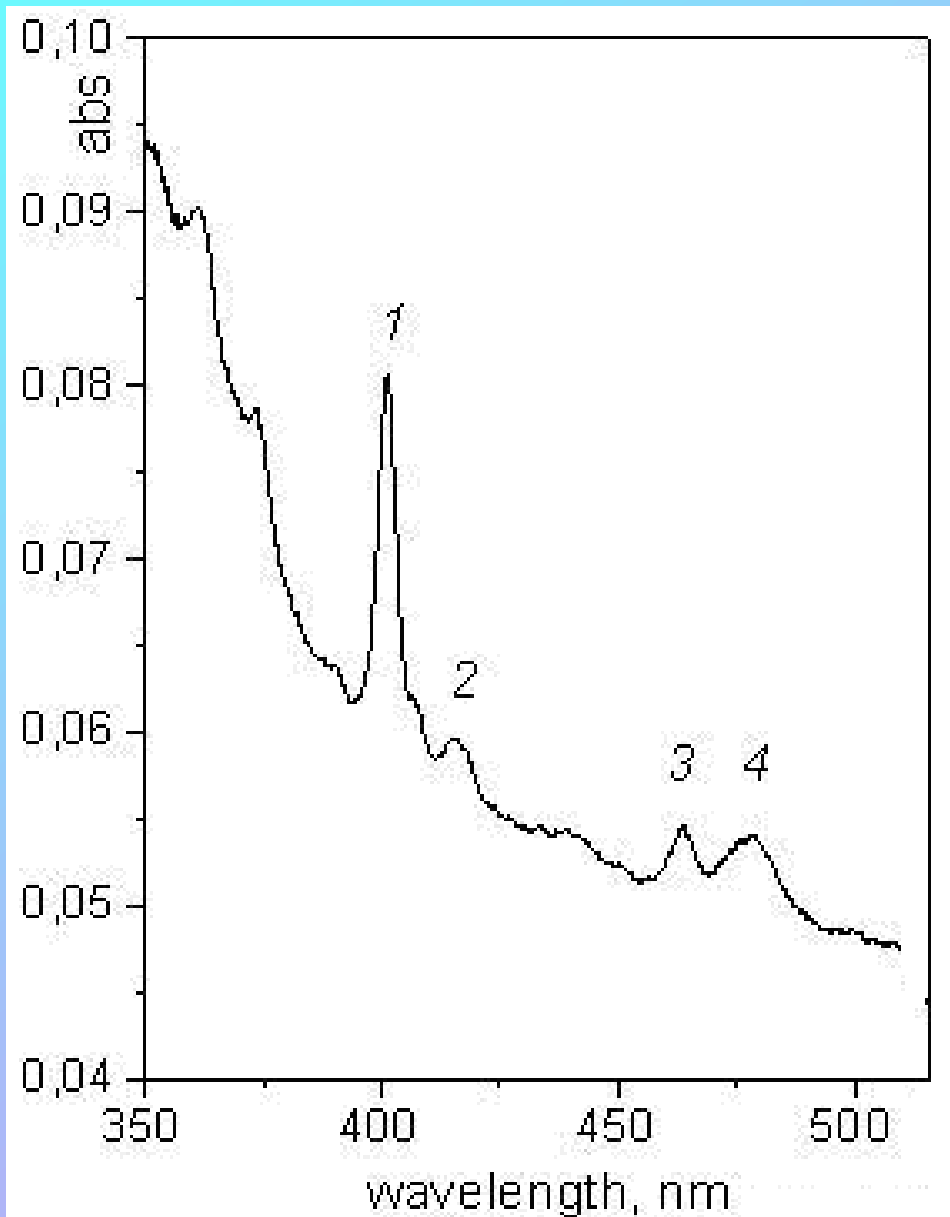
Kinetic curve of luminol chemiluminescence induced by excited plutonyl complexes



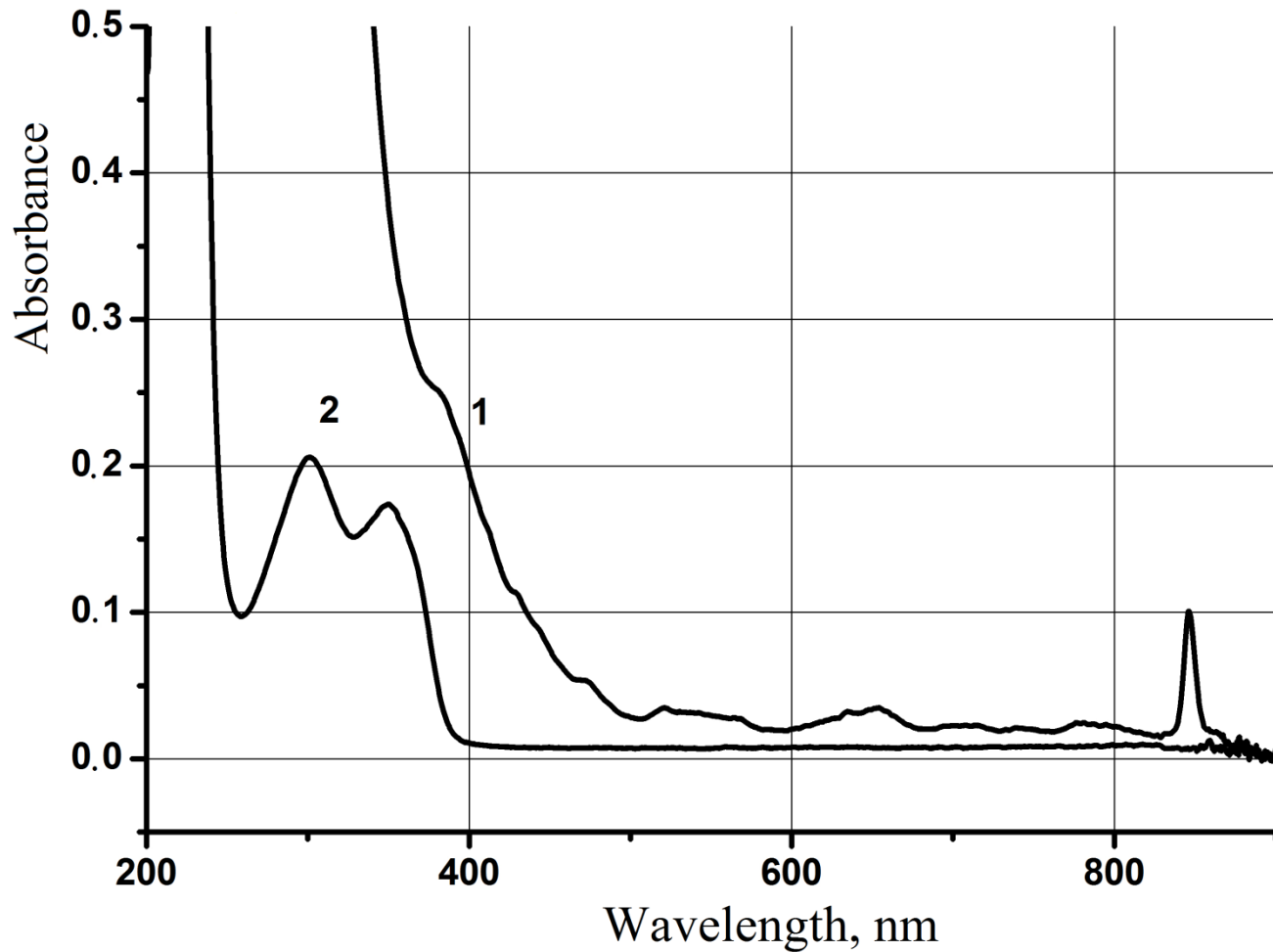
Absorption spectra of hydrated plutonium ions for various valent species



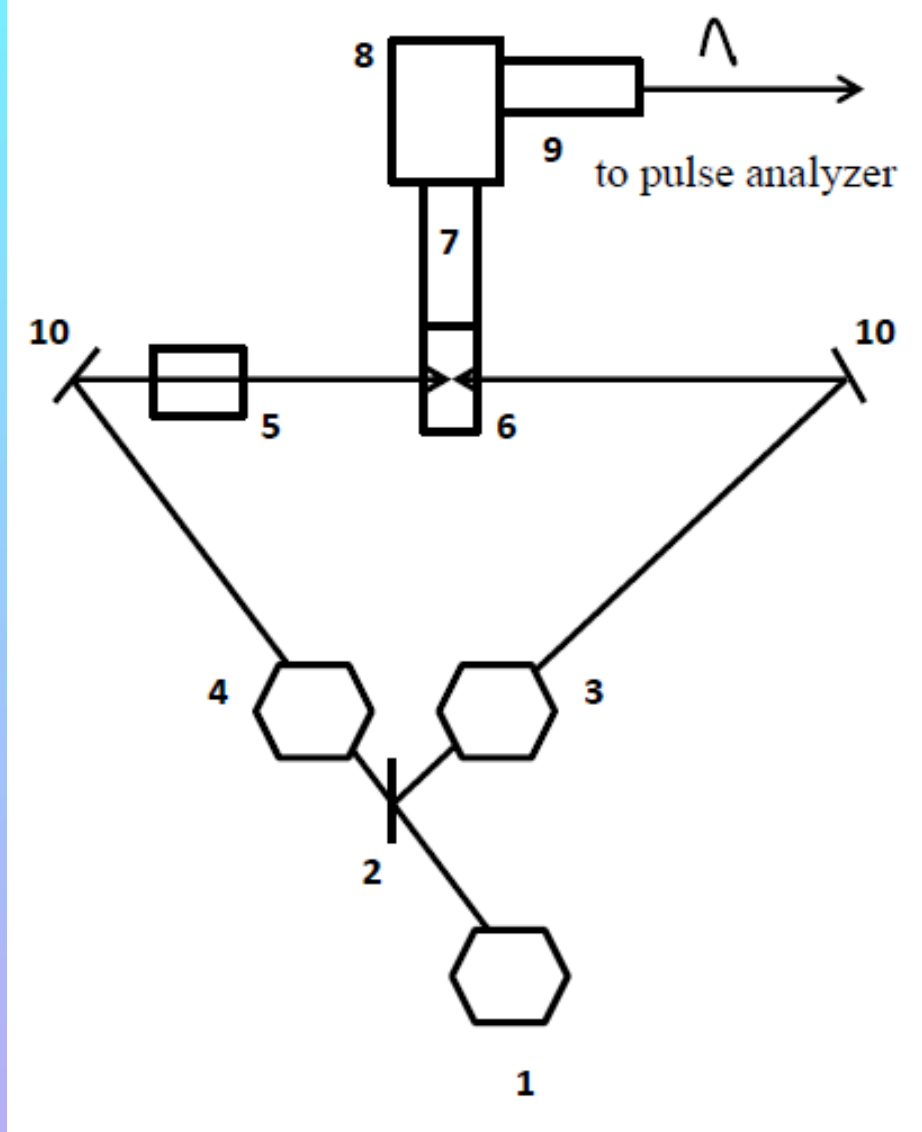
Absorption spectra of plutonyl complexes in 42 % CsF + H₂O solutions at different pH values. Two complexes are in solution: PuO₂F₅³⁻ (band 839nm) and PuO₂F₄OH³⁻ (band 846.5nm)



Absorption spectrum of aqueous solution 10^{-3} M SmCl_3 + $2 \cdot 10^{-5}$ M luminol: (1) 401.0, (2) 415.0, (3) 464.0, **(4) 477.5 nm.**



Absorption spectra of 1- PuO_2^{2+} (0.006M), and 2-luminol in 42%CsF + H_2O solution at pH=10.

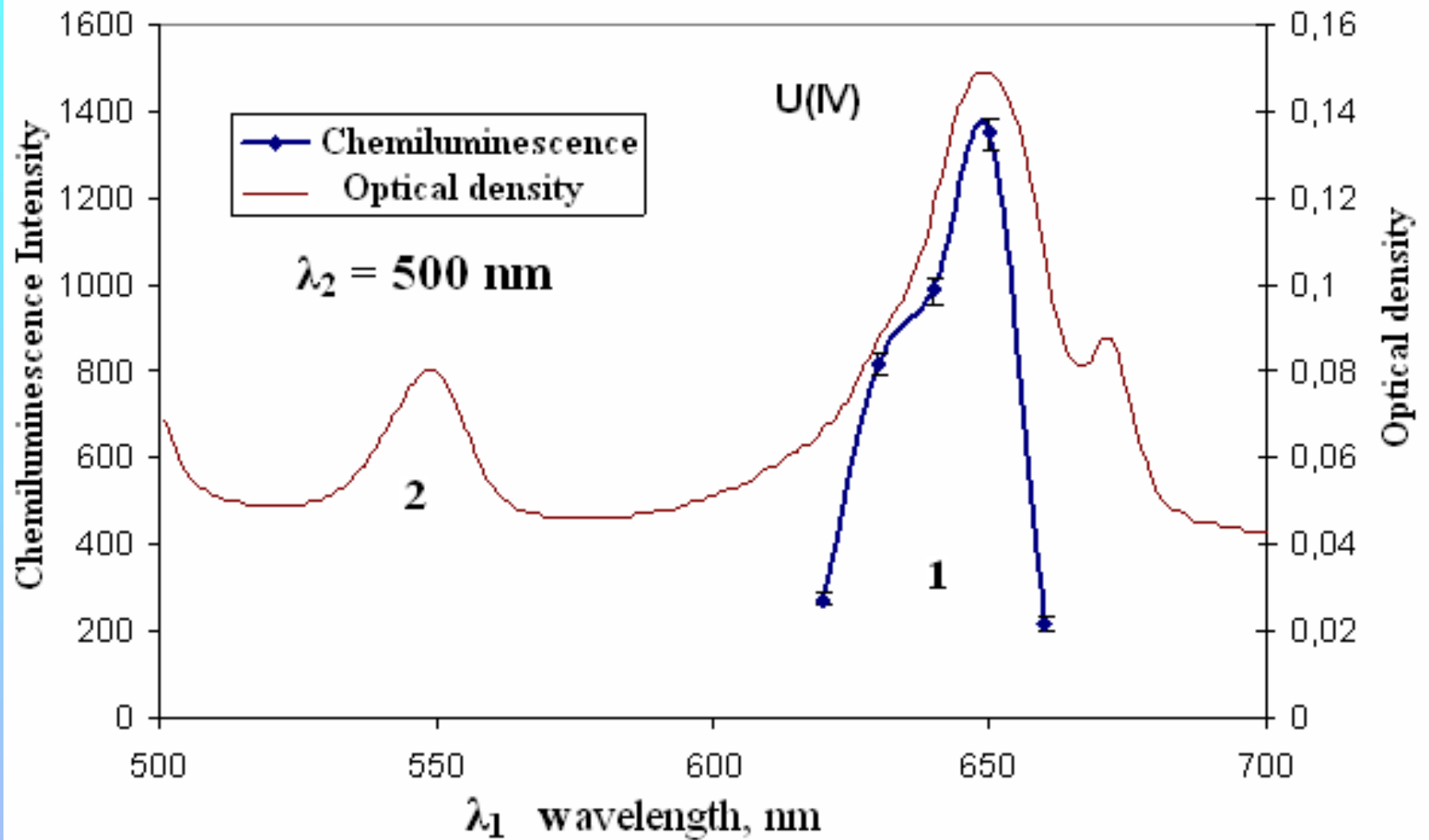


(1) nitrogen laser OBB-1010, (2) beam splitter, (3) dye laser OBB-1011, (4) dye laser OBB-1012, (5) optical delay line OPD-1, (6) cuvette with solution, (7) optical fiber, (8) monochromator DMR-4, (9) photomultiplier, (10) mirror

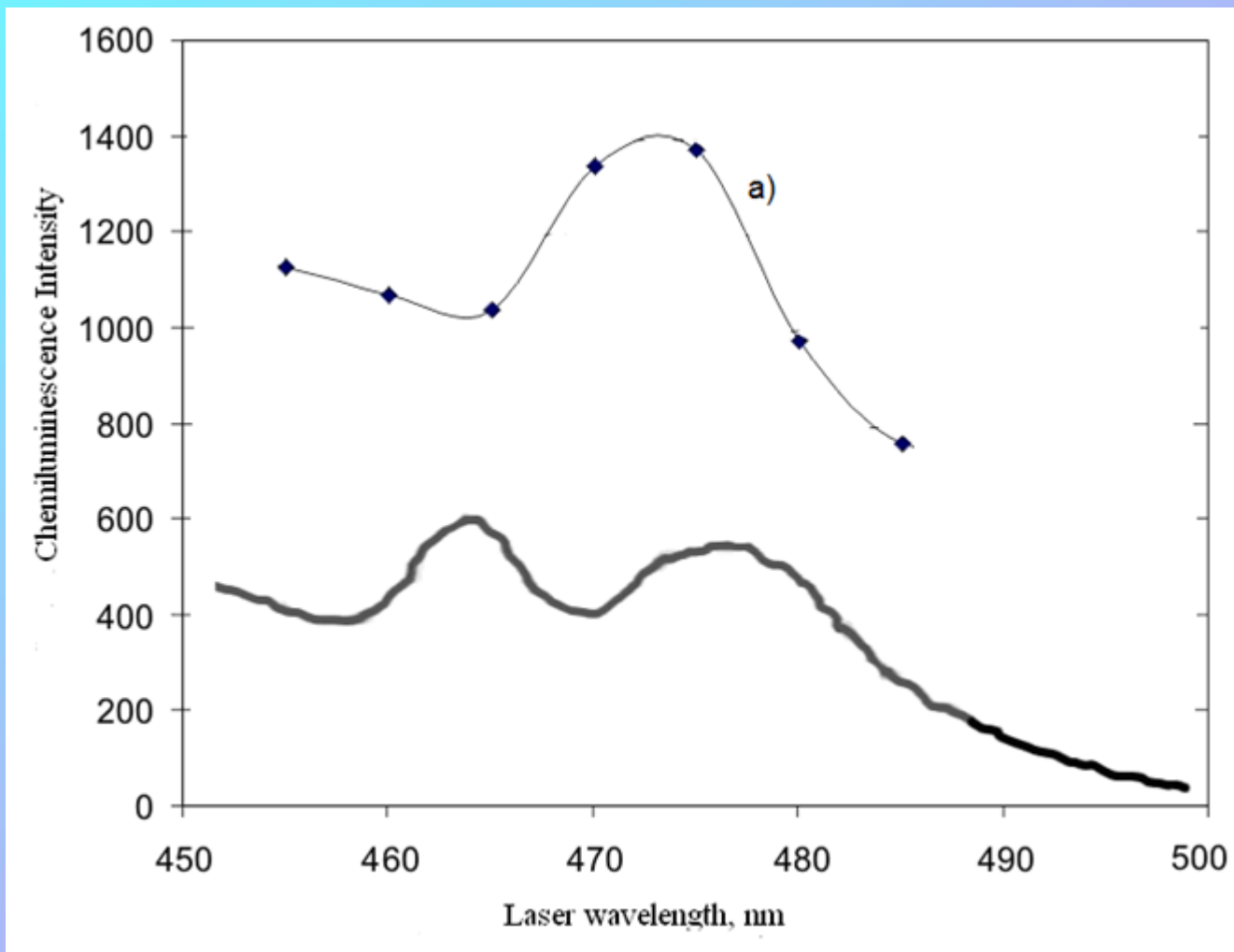


Experimental set-up for chemiluminescence spectroscopy of actinides in aqueous solutions

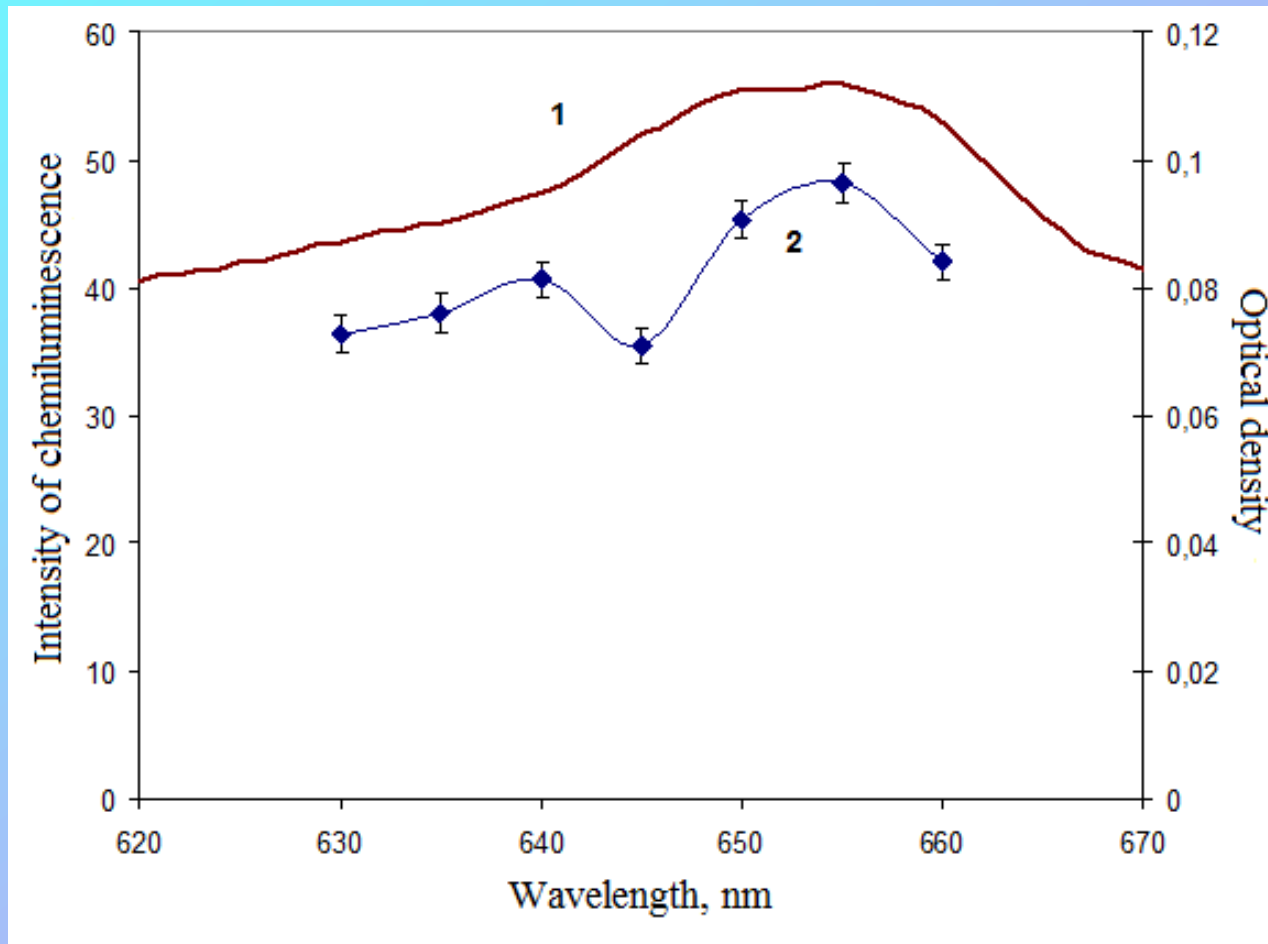




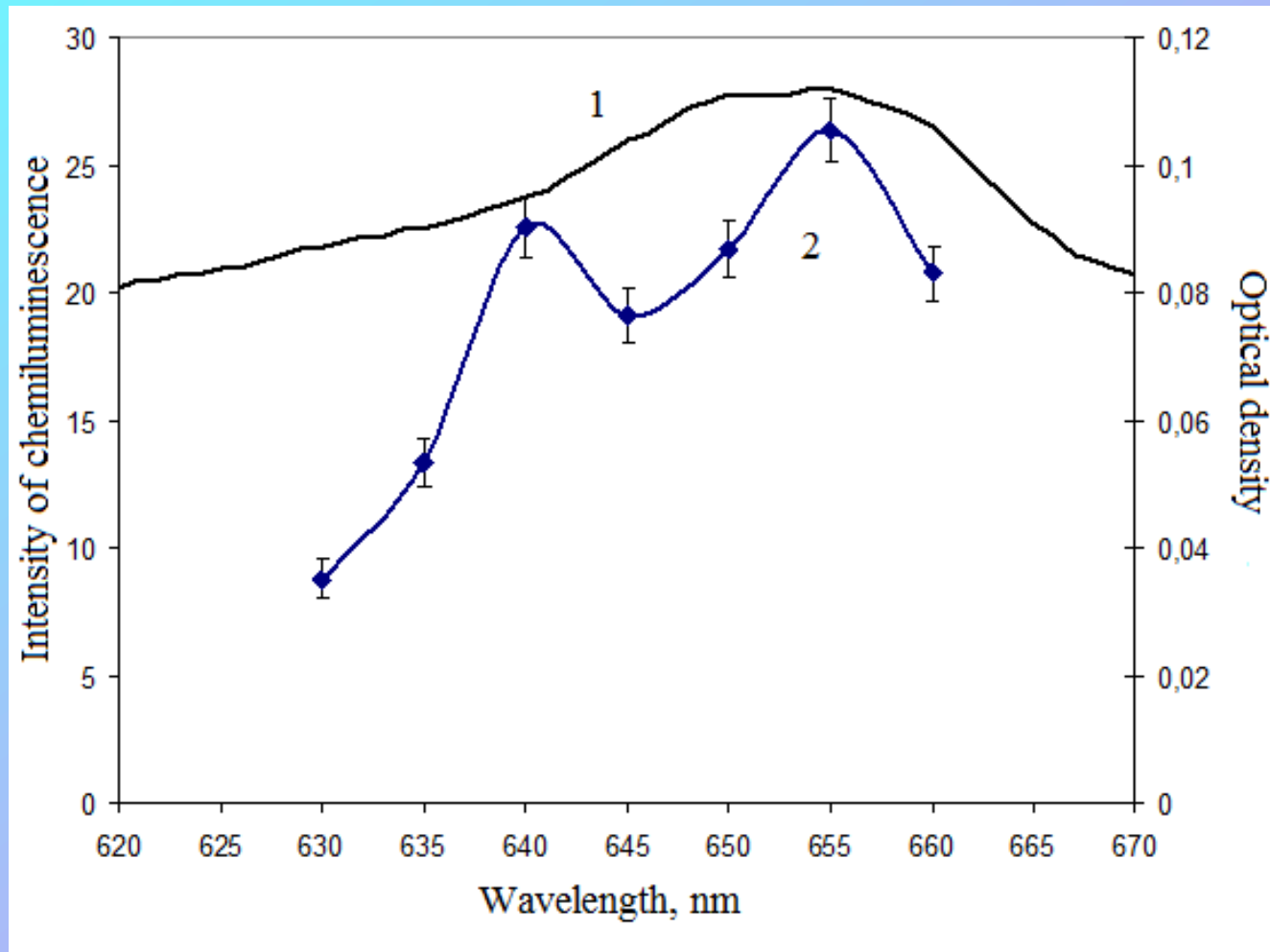
1. Luminol+U(IV)+HCl. Chemiluminescence intensity dependence on the wavelength of laser radiation at the first excitation step. When the wavelength of laser radiation corresponds to the wavelength of U(IV) absorption band than the intensity of luminal chemiluminescence is increased. The wavelength of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



Spectrum of excitation of luminol chemiluminescence (a) with dye laser in the range of absorption bands of Sm^{3+} (two steps-one color scheme). Chemiluminescence is recorded at the wavelength of 460 nm. Absorption spectrum of Sm^{3+} is shown below.

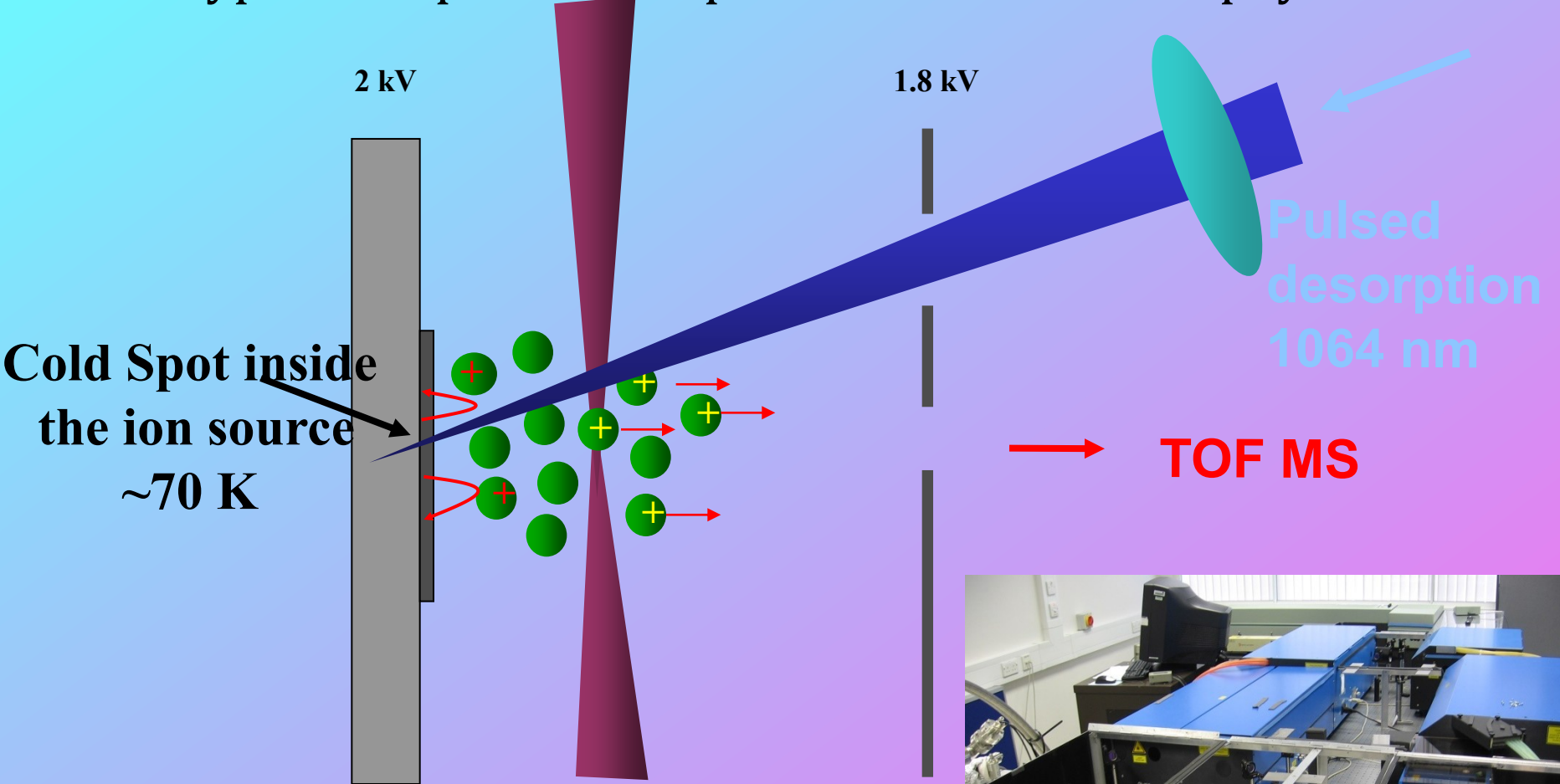


- 1-Absorption spectrum of the solution to be irradiated.
- 2-Specific intensity of chemiluminescence of Pu(IV) solution as a function of wavelength of radiation generated by the first laser, wavelength of radiation generated by the second laser 500 nm (two steps-two colors scheme). Solution composition: CsF 3.6 M, luminol 10^{-5} M, Pu(IV), solution pH was adjusted by addition of CsOH.

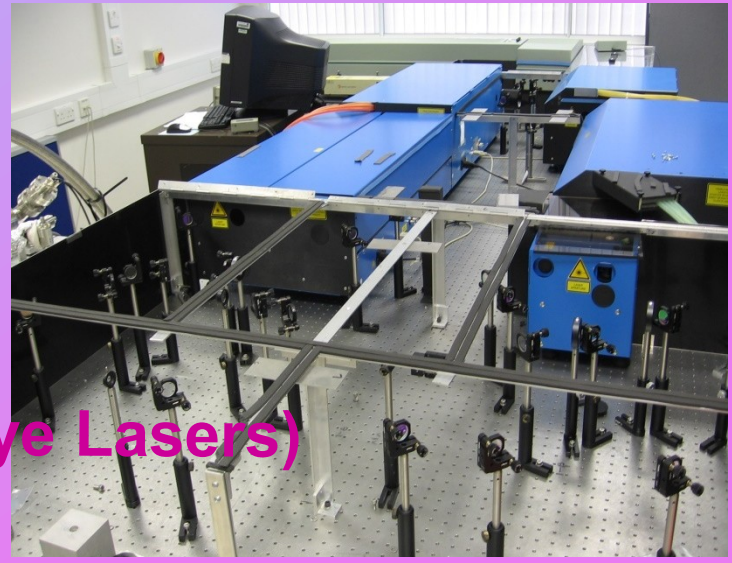


Specific intensity of chemiluminescence excited by the mechanism two steps—one color in irradiation of Pu(IV) solution by laser OBB 1012 in the range of 630-660 nm.

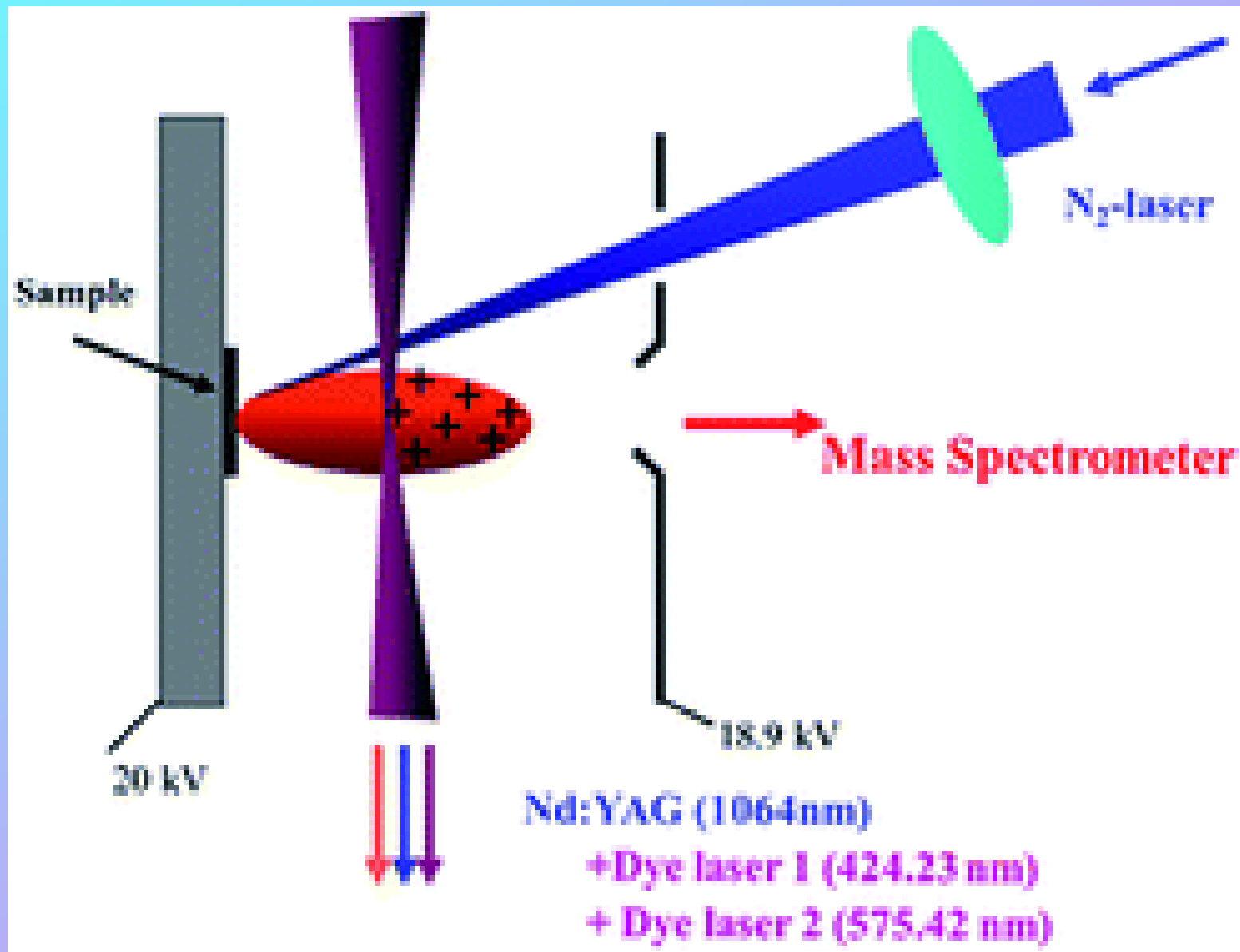
Laser Resonance Photoionisation Mass Spectrometry- Krypton isotopes for non proliferation and astrophysics.



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



MALDI-TOF mass spectrometer has been combined with a tunable ns-pulse laser ionisation system consisting of two dye lasers pumped by the second (532 nm) and the third (355 nm) harmonics of a Nd:YAG laser. Uranium samples in the form of solutions, suspensions or small solid grains can be placed onto an aluminium substrate without the MALDI matrix from which they are desorbed by a 337 nm nitrogen laser with a spatial resolution of ~ 20 μm . Highly selective and efficient uranium photoionisation schemes have been developed. They are three-colour, two-step photoionisation schemes involving resonance excitation from the ground state by a 424.23 nm laser (~ 1 μJ per pulse) and subsequently by either 578.48 nm, 575.42 nm or 574.10 nm lasers (~ 20 μJ per pulse) with 1064 nm (>1 mJ) ionisation into the continuum. A series of measurements of reference materials with concentrations between 10^{10} and 10^{16} atoms per sample (10^{-15} to 10^{-7} g) and various isotope compositions ranging from depleted and natural to enriched uranium positively confirm the method applicability. For instance, for the samples of depleted uranium the $^{235}\text{U}/^{238}\text{U} < 0.003$ ratio was determined with $<7\%$ precision (2σ errors) *for the total uranium concentrations not exceeding ~ 80 fg per sample.*



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

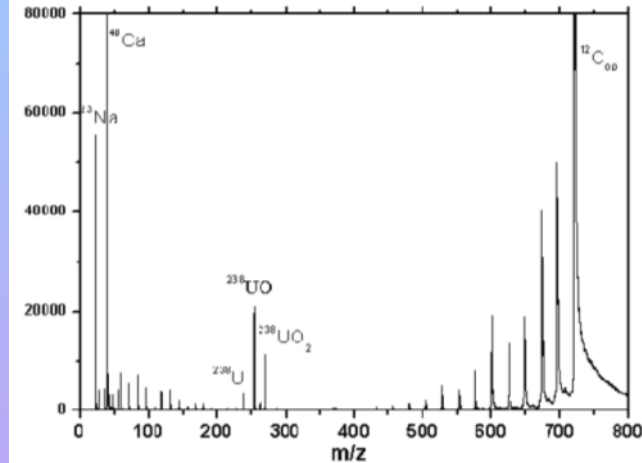


Bruker ETP, MS/MS, ESI

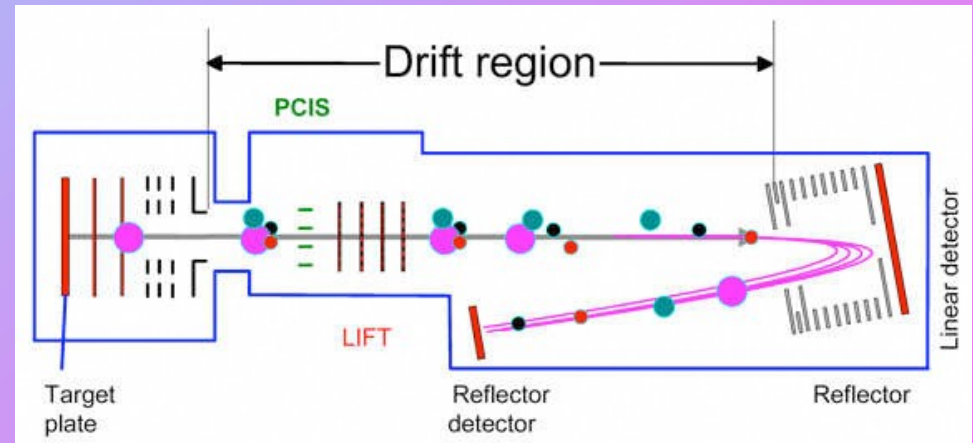
MALDI - TOF mass spectrometry: analysis of particles



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.

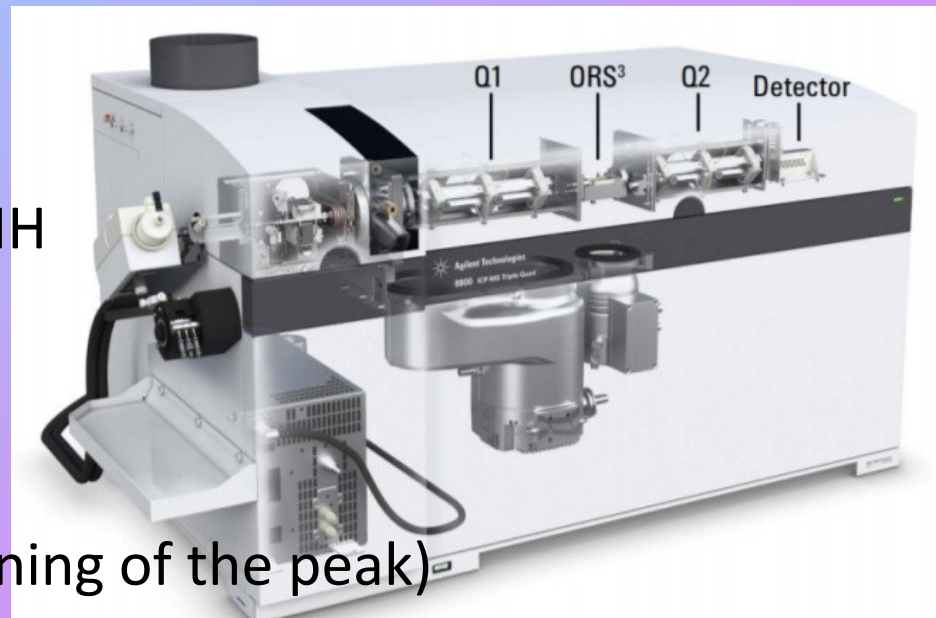


Matrix Assisted Laser Desorption Ionisation Mass spectrometry (MALDI) – mixing (usually biomolecules of very high masses with Organic matrix allowing soft ionisation reducing or completely eliminate their fragmentation.

Schmatzu MALDI TOF mass spectrometer

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

ICP-QQQ, ICP-MS/MS, Agilent 8900 ICP-QQQ

Agilent

The Agilent 8900 ICP-QQQ redefines ICP-MS performance. Tandem ICP mass spec operation (ICP-MS/MS) makes this the world's most powerful and flexible multi-element analyzer.

Typical ICPMS software: Agilent “Mass Hunter 4”

Regarding polyatomic/molecular interferences, it is not a problem with the modern ICPMS technology. The mass spec. uses a reaction cell (filled with O₂, H₂ or NH₃)- and two quadrupoles - MS/MS mass spectrometry. E.g. first one is tuned to Fe -> reaction FeO -> the second quadrupole is detecting FeO.

Second mode is the collision cell. This one is filled with He. ²³⁸U and ²³⁹Pu (the same mass) will enter the He cell. But the mean free path will be different (longer) for ²³⁸U than for ²³⁹Pu. On the mass spec you will see two different peaks. Even with the very large ratios the contribution is <1% in He mode.

- In this work we have applied both INAA and ICP-MS methods 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.
- A reasonable agreement between the two methods has been observed, with expected better precision of ICP-MS for some trace elements, and INAA as being more suitable for bulk analysis of e.g. Na, Ca and P.
- The correlation of the bone/soil elemental ratio with the age of the sample (accumulation coefficients or mobility) of several elements have been studied. The most accumulated elements are U, Zn, Sr, and lanthanides which can be due to either a long period of time the samples spent in the soil or attributed to some anomalous phenomena in the past. Cr, Co, and Ba are least mobile elements.
- **A high concentration of uranium we detected in the bones of dinosaurs (122 mg/kg), South mammoth (220 mg/kg), prehistoric bear (24 mg/kg) and archanthropus (1.5 mg/kg) compared to surrounding soils (3.7-7.8 mg/kg) and standard bones (<0.01 mg/kg) is a bit of a puzzle. The uranium fission elements (La, Ce Nd, Sm, Eu, Tb, Yb, Lu, As, Br and Mo) have been also detected in these bones.**
- **^{234}U concentration differ from secular equilibrium**

Sample 1 – South mammoth bone found in Angren;

Sample 2 – Soil near the bone, Angren;

Sample 3 - South mammoth bone found in Kashkadari;

Sample 4 – Kashkadari Soil near found bone;

Sample 5- KA-arhantrope bone;

Sample 6 – bone of bear from Selungur cave

Sample 8 – Dinosaur bone-2

Sample 7 – Dinosaur bone 1,

Sample 9 – standard bone;

Sample 10 – soil near the standard bone;

Sample 11 - Soil near Dinosaur bone 1.

The secular equilibrium lies in the fact that the number of decays (activity) of all members of the radioactive series is equal to each other, and if the initial isotope has a very long lifetime (constant activity), then no change in the activity of the daughter radioactive elements is observed. With sufficient accuracy, it can be assumed that the secular equilibrium occurs in a time equal to ten times the half-life of the longest-lived element: **in the uranium decay chain — after 830000 years**

^{238}U (99.28%) + ^{235}U (0.72%) + ^{234}U (0.0055%) – $2.5 \cdot 10^4$ Bq/g natural uranium.

^{238}U - $1.25 \cdot 10^4$ Bq/g. ^{235}U - $8 \cdot 10^4$ Bq/g. ^{234}U - $230 \cdot 10^6$ Bq/g.

^{234}U - member of ^{238}U decay chain

natural radioactivity N : $^{238}\text{U} \approx ^{234}\text{U} \approx 21x^{235}\text{U}$ or $N \approx 2 \cdot ^{238}\text{U}$ Bq.

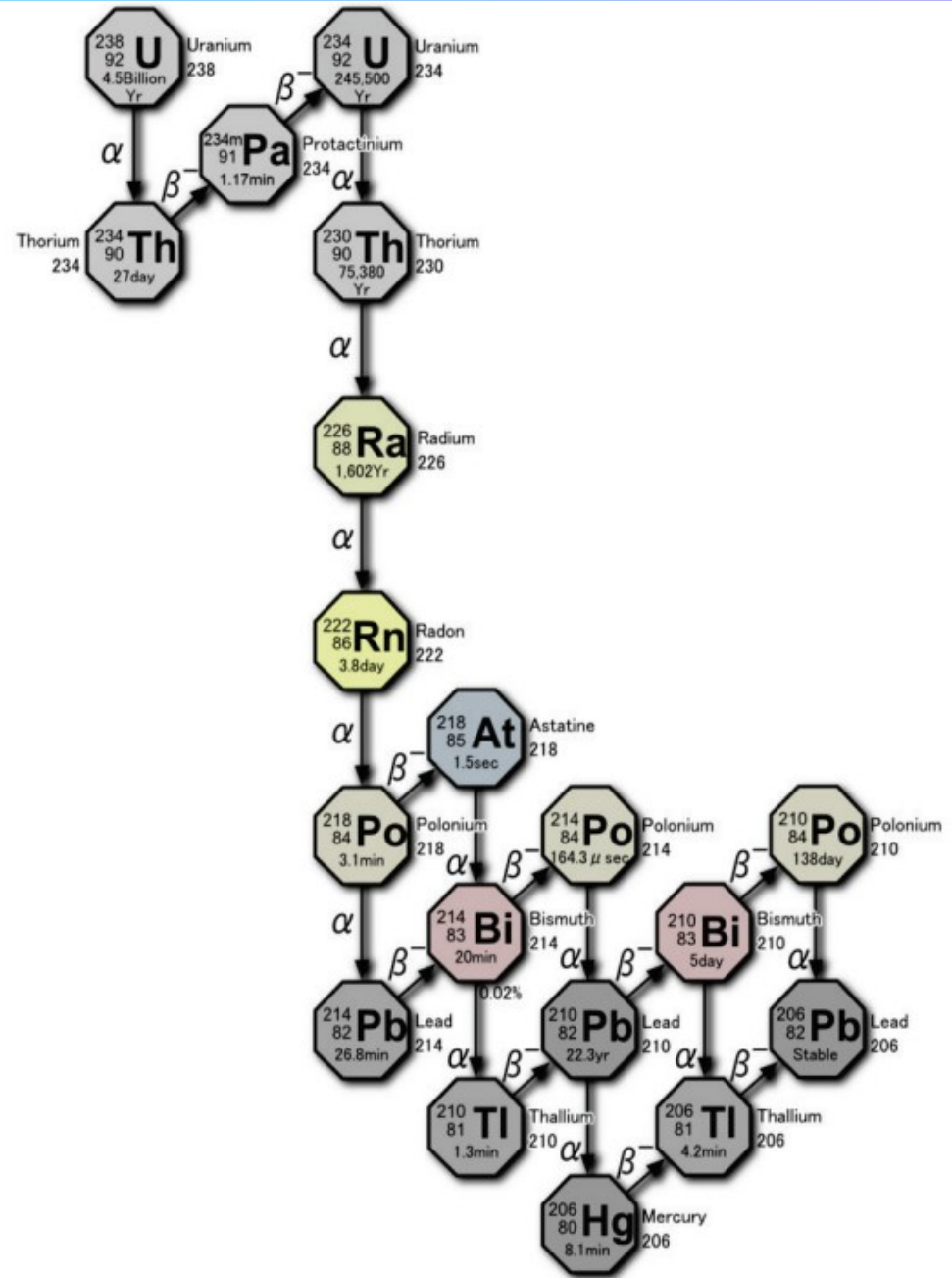
1.00 gram of uranium, the uranium-238 decays at a rate of **12500 nuclei per second** into thorium-234. The thorium-234 in the rock also decays at a rate of 12500 nuclei per second into protactinium-234. The protactinium-234 in the rock also decays at a rate of 12500 nuclei per second into uranium-234, and so on down the chain, which ends with lead-206, a stable element that accumulates at a rate of 12500 nuclei per second, without any further decay.

$^{238}\text{U} \rightarrow ^{234}\text{Th} \rightarrow ^{234}\text{Pa} \rightarrow ^{234}\text{U} \rightarrow ^{230}\text{Th} \rightarrow ^{226}\text{Ra} \rightarrow ^{222}\text{Rn} \rightarrow ^{218}\text{Po} \rightarrow ^{214}\text{Pb} \rightarrow ^{214}\text{Bi} \rightarrow ^{214}\text{Po} \rightarrow ^{210}\text{Pb} \rightarrow ^{210}\text{Bi} \rightarrow ^{210}\text{Po} \rightarrow ^{206}\text{Pb}$

^{234}U concentration differ from secular equilibrium – in samples higher concentration (due to ^{234}Th and ^{234}Pa chemistry? or due to ^{234}Th track behavior in track after alpha decay of ^{238}U ?)

238U decay chain

$A = 4n + 2$: $^{238}\text{U} \rightarrow ^{206}\text{Pb}$,



High concentration of uranium is a bit of a puzzle.

One of the reasons may be the presence of a uranium sorbent in the bones. Phosphorus 12-20% was detected of in prehistoric and ancient bones by the ICP-MS method.

Insoluble **phosphate compounds** (possibly tricalcium phosphate or mineral apatite phosphate), which is the **main sorbent of uranium in bones?**, may be connected with phosphorus detection.

^{234}U concentration differ from secular equilibrium – in samples higher concentration (due to ^{234}Th and ^{234}Pa chemistry?)

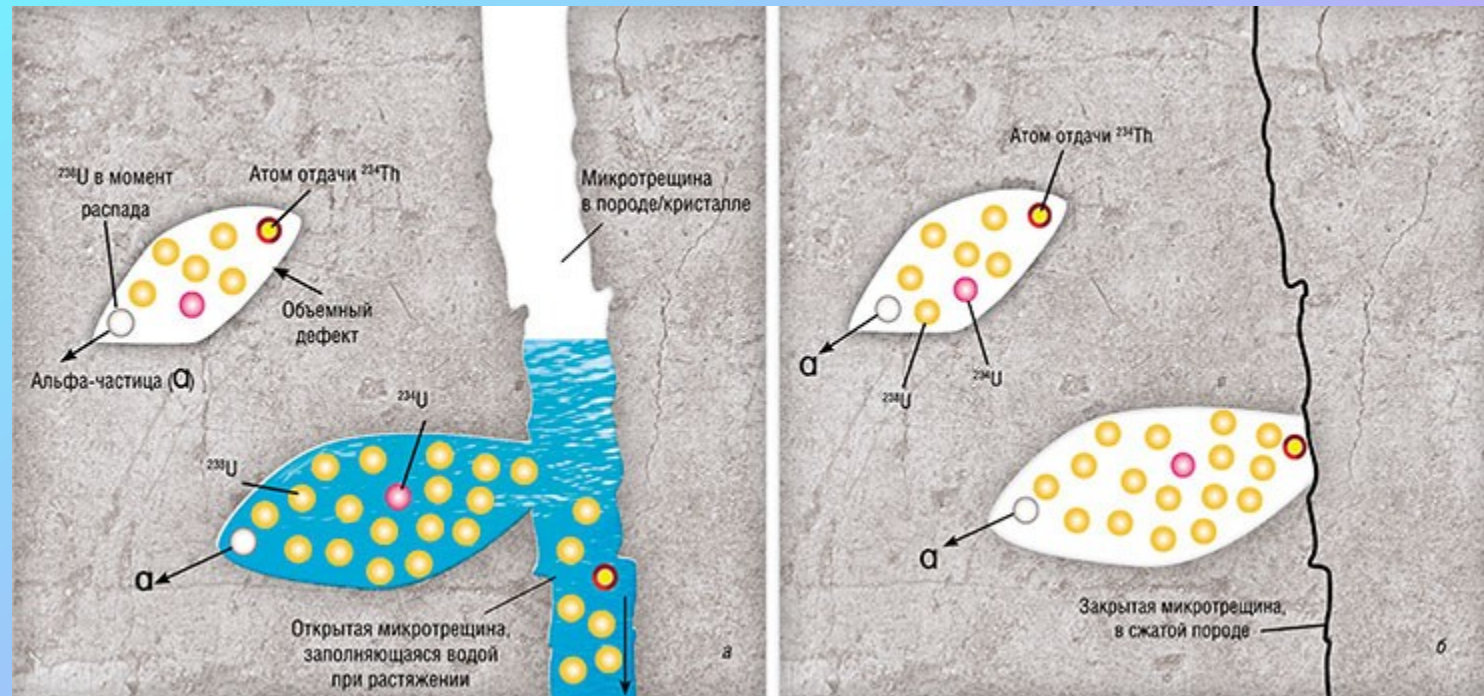
Future Plans

1. Complete processing and analysis of the bones ICP-MS spectra
2. Experiments with rock paintings
3. Combination with Accelerator Mass Spectrometry

Conclusion

- Luminescence (TRLIF) and Chemiluminescence (TRLIC):
LOD up to 10^{-9} - 10^{-13} mol/l, 1ml need for analysis.
- The resonance ionization spectroscopy in combination with mass spectrometry has been successfully used for the development of the state of the art instruments capable of detection of isotope ratios at **fg-level**.
- TRLIF/TRLIC as well as RIMS method with laser ionisation mass spectrometry methods allows one to obtain more complete information about the sample.
- We have applied both INAA and ICP-MS methods 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. Better precision of ICP-MS for some trace elements, and INAA as being more suitable for bulk analysis of e.g. Na, Ca and P.
- **A high concentration of uranium we detected** in the bones of dinosaurs (122 mg/kg), South mammoth (220 mg/kg), prehistoric bear (24 mg/kg) and archanthropus (1.5 mg/kg) compared to surrounding soils (3.7-7.8 mg/kg) and standard bones (<0.01 mg/kg) **is a bit of a puzzle**. The **uranium fission elements** (La, Ce Nd, Sm, Eu, Tb, Yb, Lu, As, Br and Mo) have been also detected in these bones.
- **^{234}U concentration differ from secular equilibrium – in samples higher concentration (due to ^{234}Th and ^{234}Pa chemistry? or due to ^{234}Th behavior in track after alpha decay of ^{238}U ? , connected with the Cherdyntsev — Chalov effect – ^{234}Th recoil + water in and near track?)**
- **Currently, the problem of ^{234}U kinetics and the formation of variations of the $^{234}\text{U}/^{238}\text{U}$ isotope ratio in natural environments remains unresolved.**

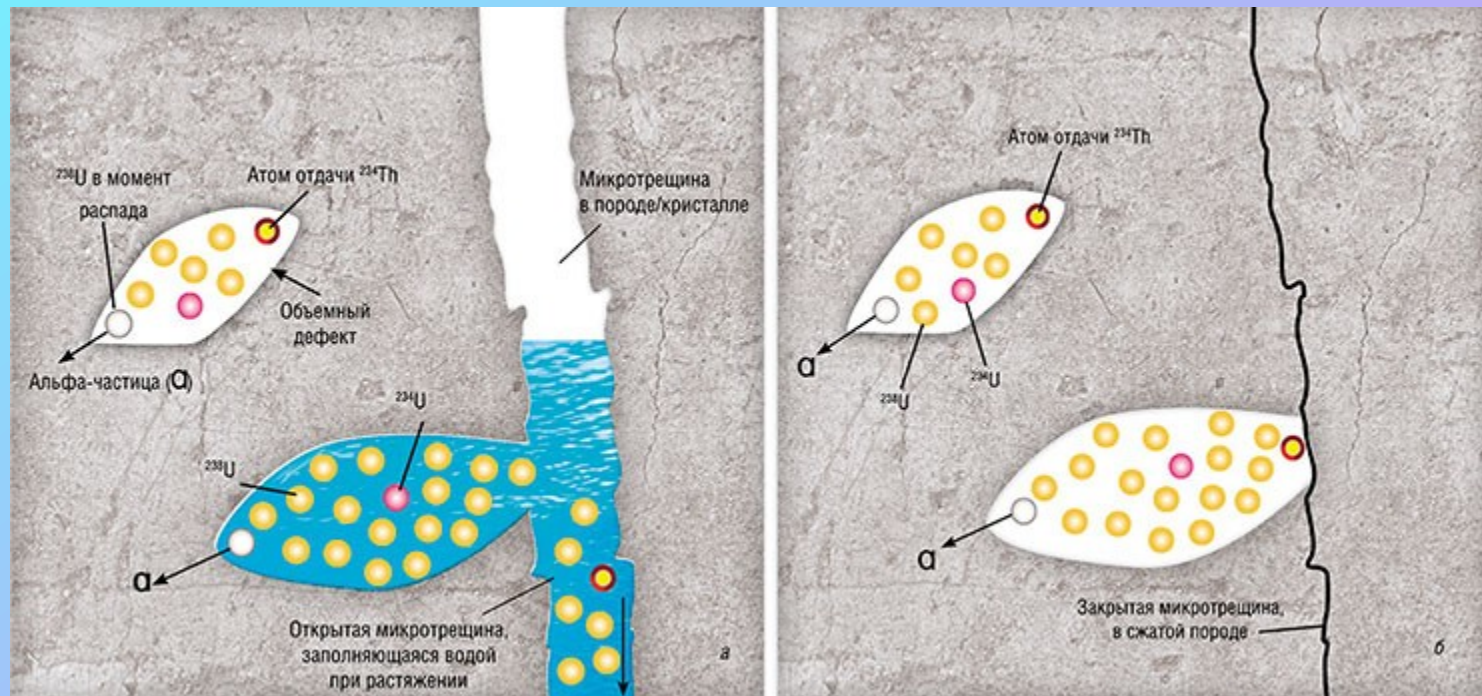
The ^{234}Th recoil nucleus breaks away from the rock when going into the water.
Cherdyntsev — Chalov effect



- **Currently, the problem of ^{234}U kinetics and the formation of variations of the $^{234}\text{U}/^{238}\text{U}$ isotope ratio in natural environments remains unresolved.**

There are excesses of the isotope ^{234}U in the total level of various minerals and rocks, the age of which significantly exceeds the period of establishment of secular equilibrium.

Ядро отдачи ^{234}Th отрывается от горной породы при переходе в воду.
Cherdyntsev — Chalov effect



В настоящее время проблема кинетики ^{234}U и формирования вариаций изотопного отношения $^{234}\text{U}/^{238}\text{U}$ в природных средах остается не решенной.

Наблюдаются избытки изотопа ^{234}U в суммарном уране различных минералов и горных пород, возраст которых значительно превышает период установления secularного равновесия.