Detection of ^{235}U and ^{238}U in solid samples using laser ablation followed by laser atomic absorption/fluorescence spectrometry.

M. Bolshov[1,2],
A. Quentmeier[2], K. Niemax[2], B. Smith[3].

[1]Institute of Spectroscopy RAS, Troitzk, Russia
[2]Institute for Analytical Science, Dortmund, Germany
[3]University of Florida, Gainesville, USA

U - lines

Atom/ Ion	λ air (^{238}U)	E_{low}	J_{low}	Log(gf)	IS (^{238}U - ^{235}U) (10^{-3} cm^{-1})
UI	387.1035	0.00	6.0	0.23	-285
UI	387.6133	0.00	6.0	-0.568	-360
UI	388.3111	0.00	6.0	-0.571	-215
UI	404.2750	620	5.0	0.052	-290
UI	404.7612	620	5.0	-0.337	-455
UI	424.6260	0.00	6.0		
UI	682.6913	0.00	6.0	-1.679	-380

For ^{238}UI: λ^{air} = 682.6913 (nm) → ν = 14647.90895 cm^{-1} λ^{vac} = 682.880 (nm)

For ^{235}UI: λ^{air} = 682.6736 (nm) → ν = 14648.28873 cm^{-1} λ^{vac} = 682.862 (nm)

$\Delta\nu^{238-235}$ = - 0.3798 cm^{-1}.

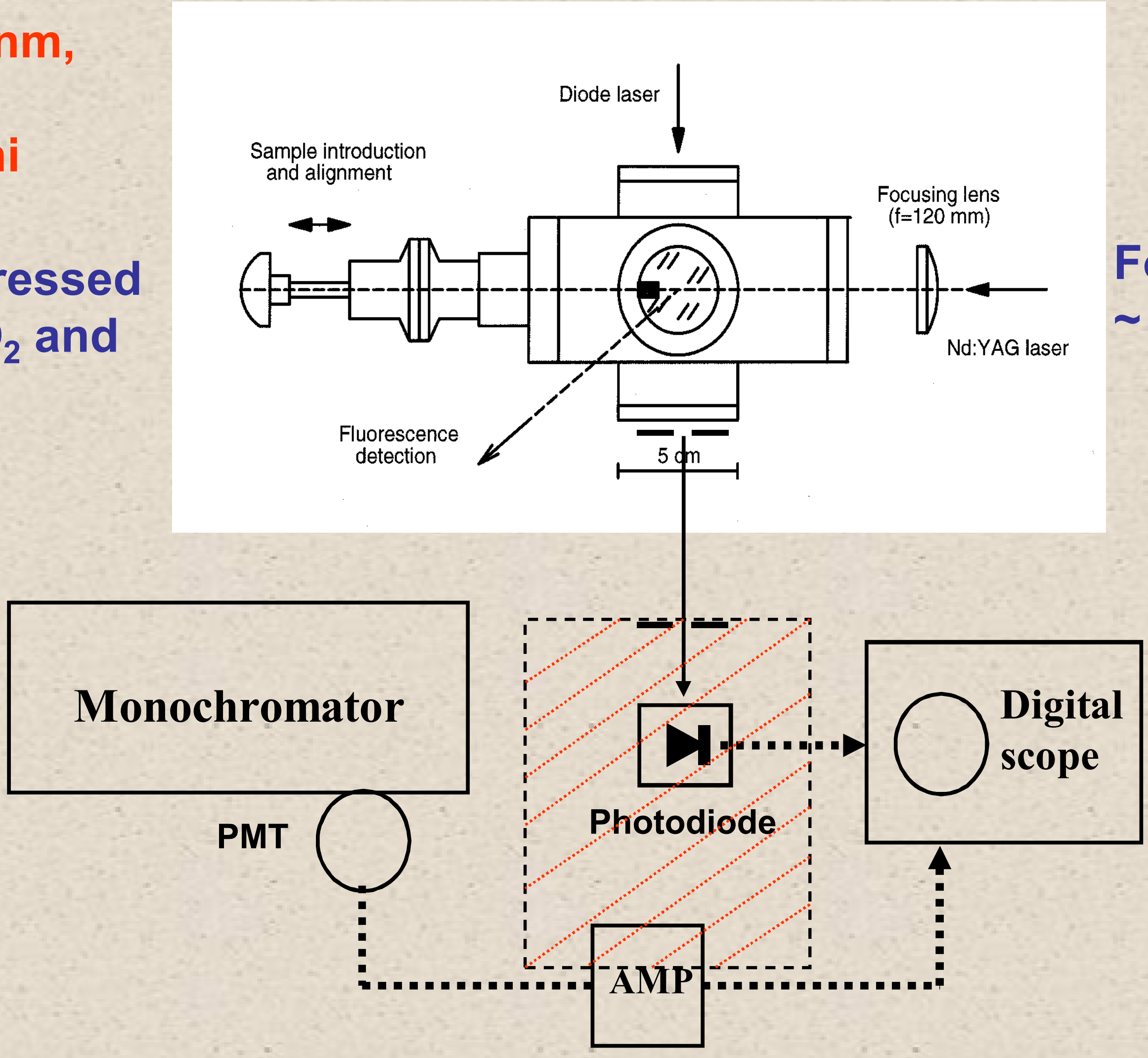
Probing of Laser Plasma by DLAAS/DLIF

	DL - AAS ("hot zone")	vs	DL – IF ("cool zone")
Advantages	Plasma emission can be effectively eliminated.		Wide linear dynamic range. Narrow lines/high resolution
Disadvantages	Poor dynamic range. Optically thick conditions for major isotope. Line broadening		Limitation by emission of laser plasma. Lower number densities

Experimental set-up

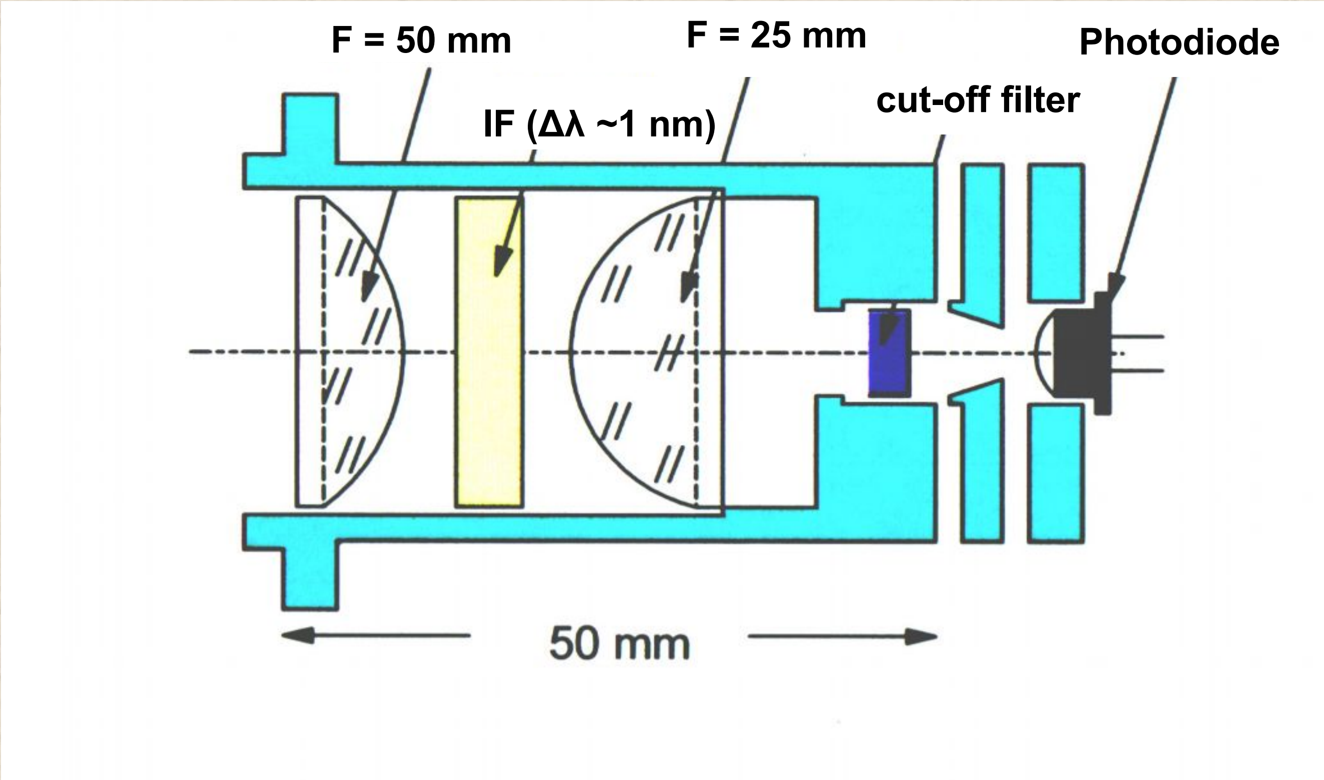
DL – 684 nm,
50 mW,
Mitsubishi

Sample – pressed pellet of UO_2 and graphite



Focal spot ~ 85 μm

Compact detection module



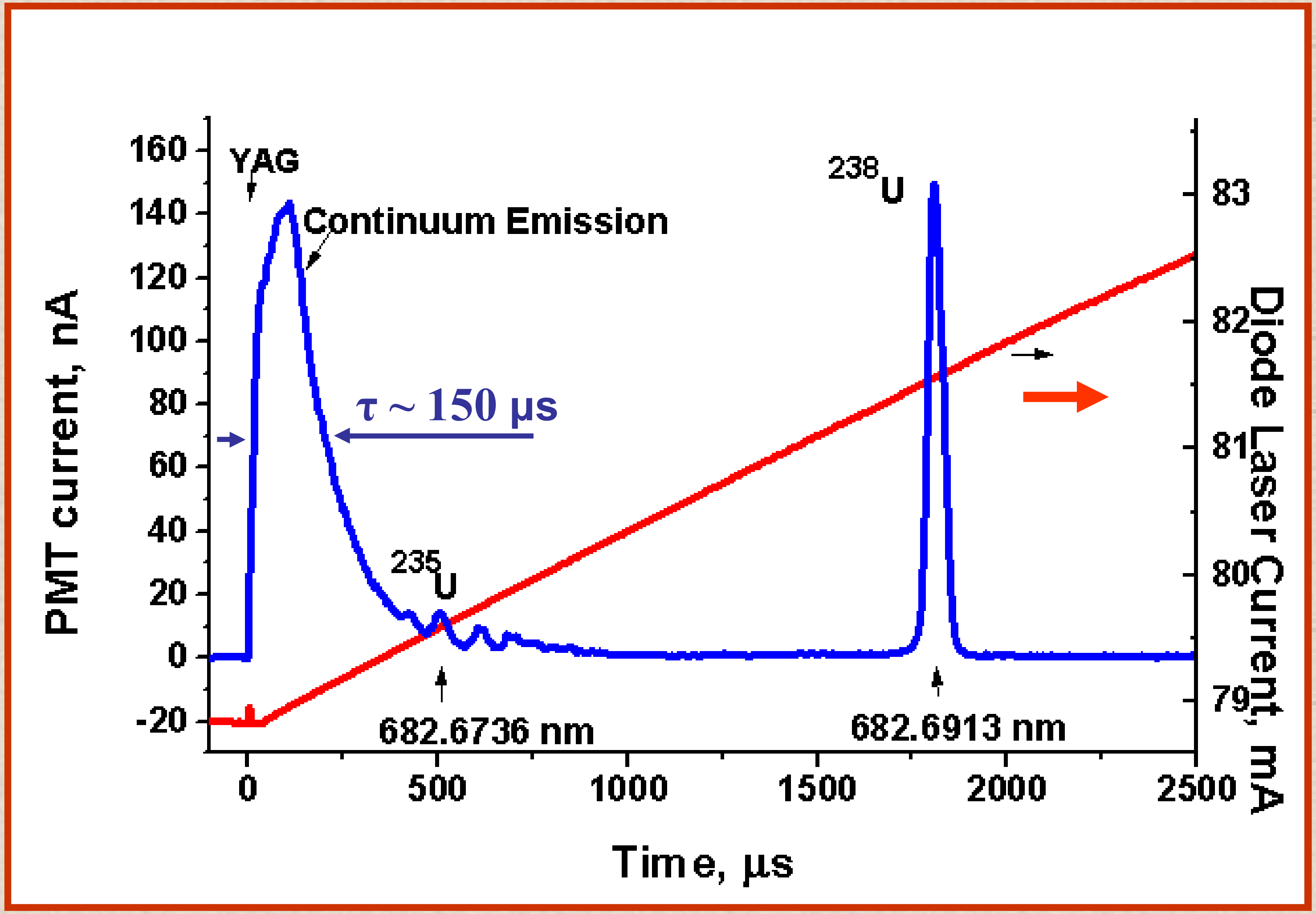
DL -- LIF. I

Scanning mode

DL wavelength is being scanned.

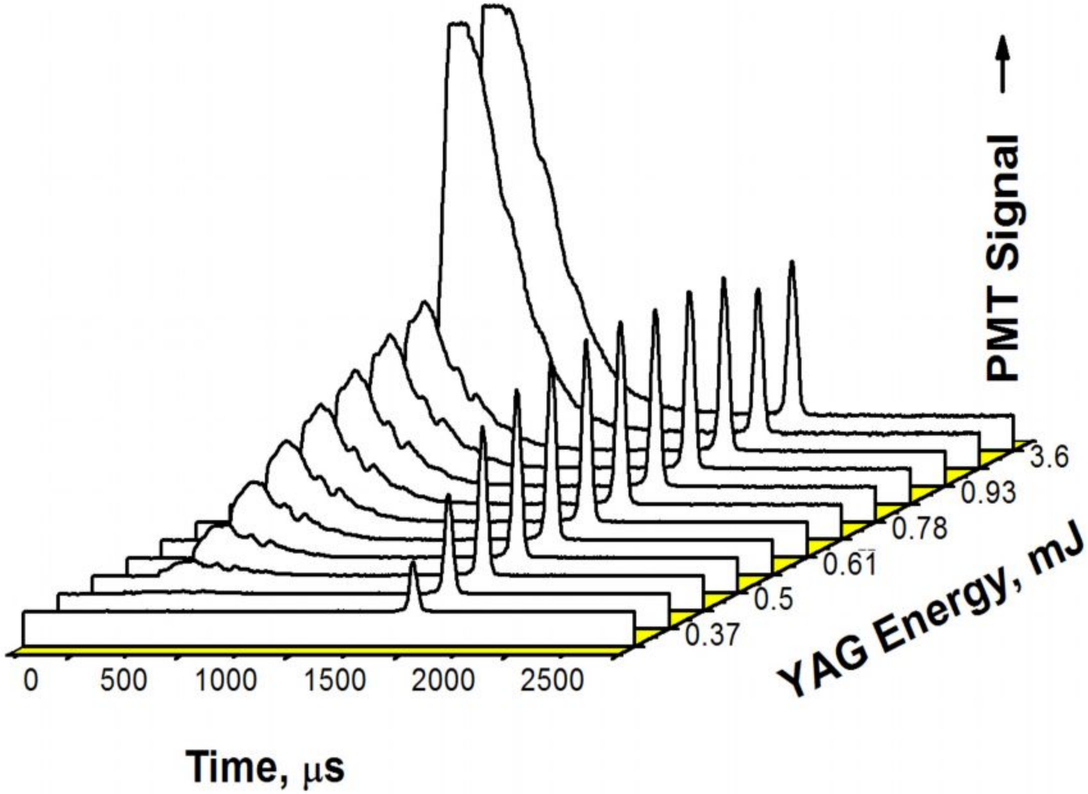
Simultaneous probing of both isotopes in each laser shot.

^{235}U and ^{238}U atomic fluorescence spectrum

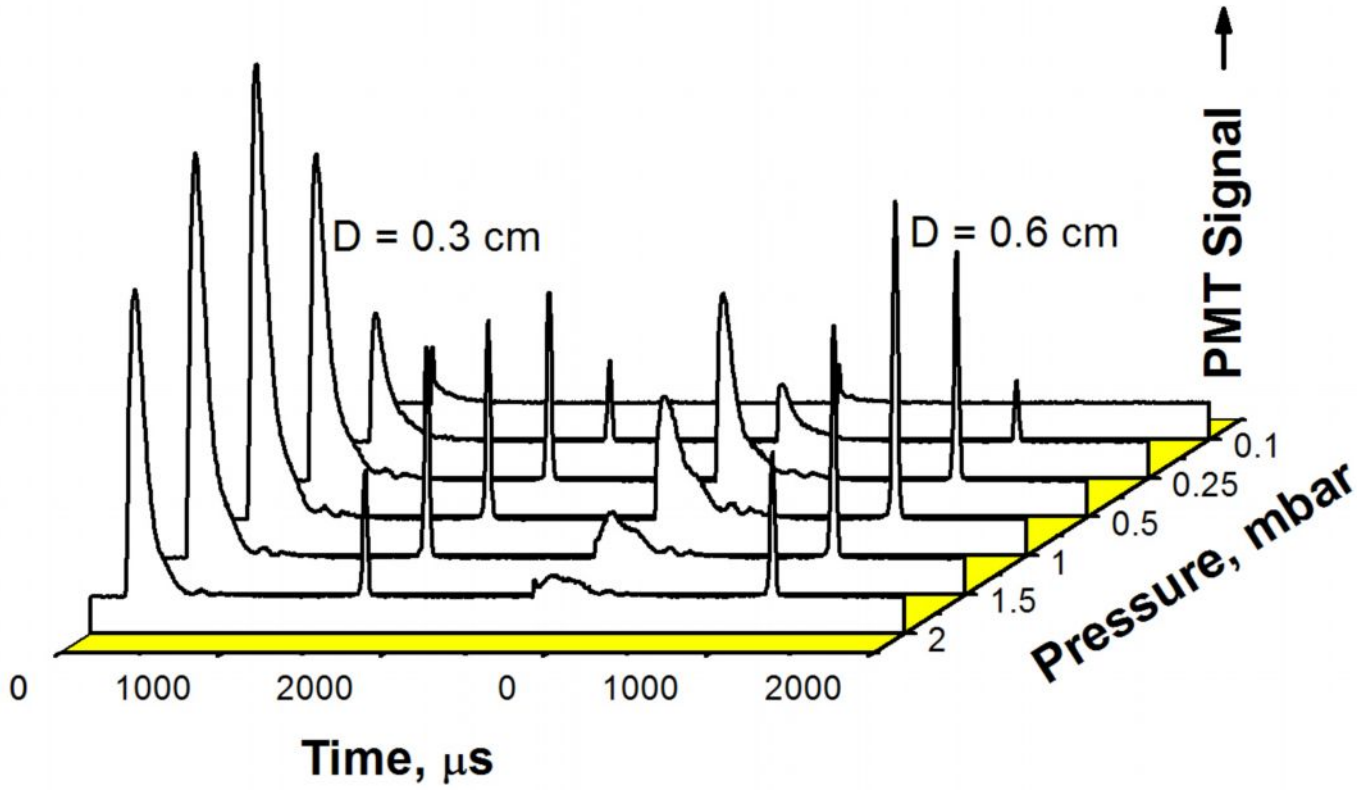


DL wavelength scanning rate ~ 0.016 pm/μs

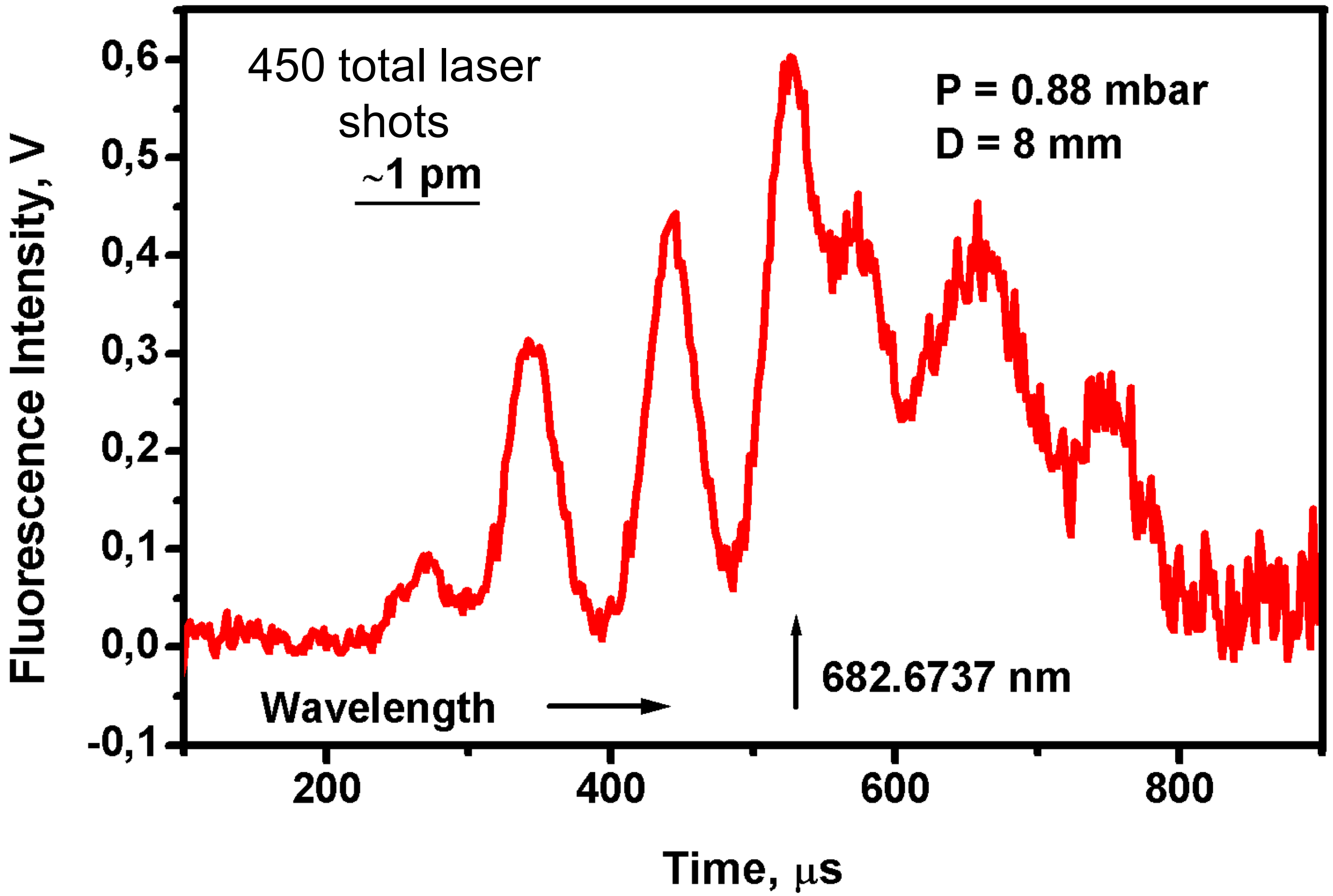
Nd:YAG pulse energy optimization



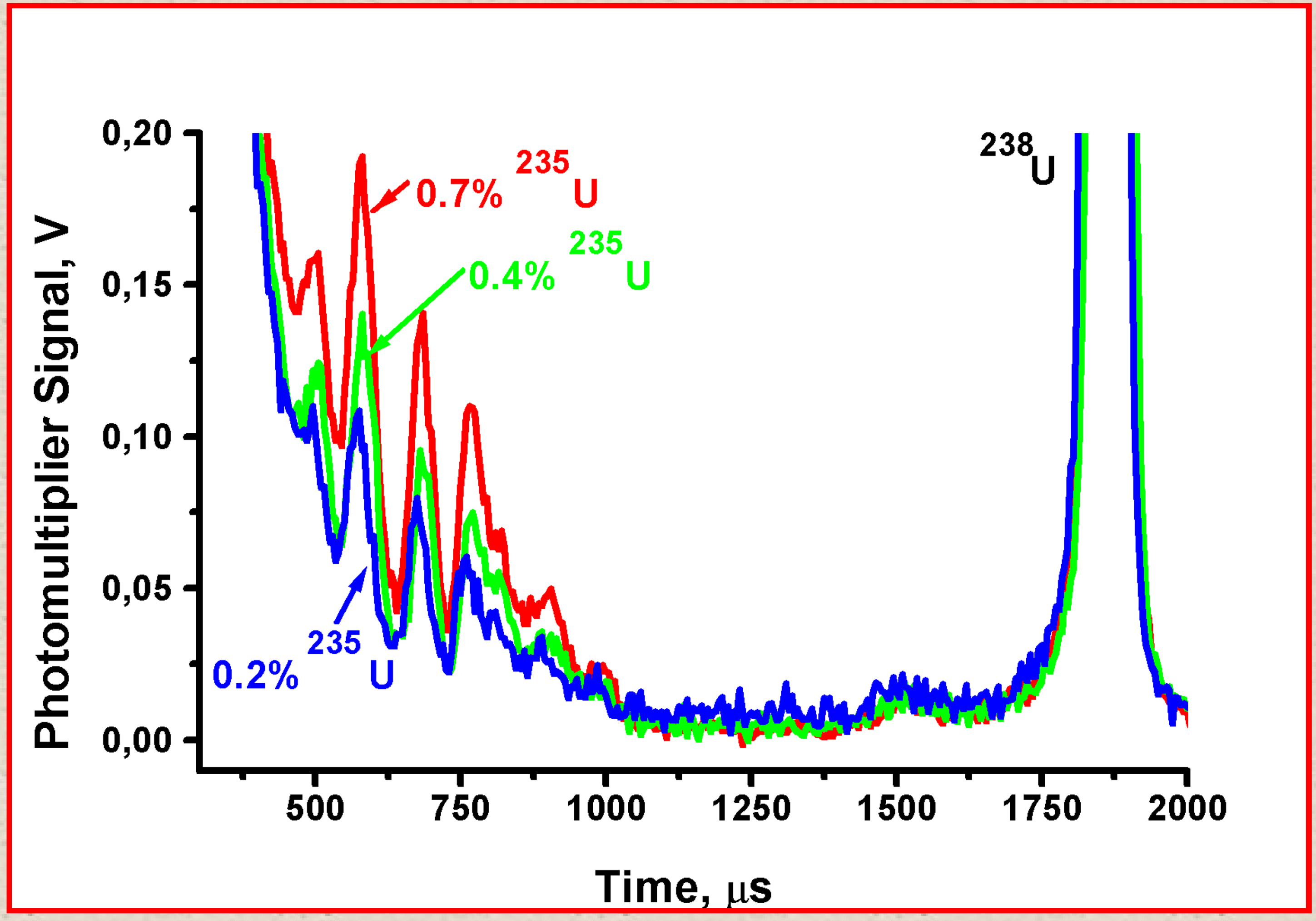
Buffer gas pressure optimization



Сверхтонкая структура линии U^{235}



Сигналы Spectra of uranium oxide samples with ^{235}U concentrations of 0.204, 0.407 and 0.714%



Each spectra is the average of 300 laser shots. No correction for emission background

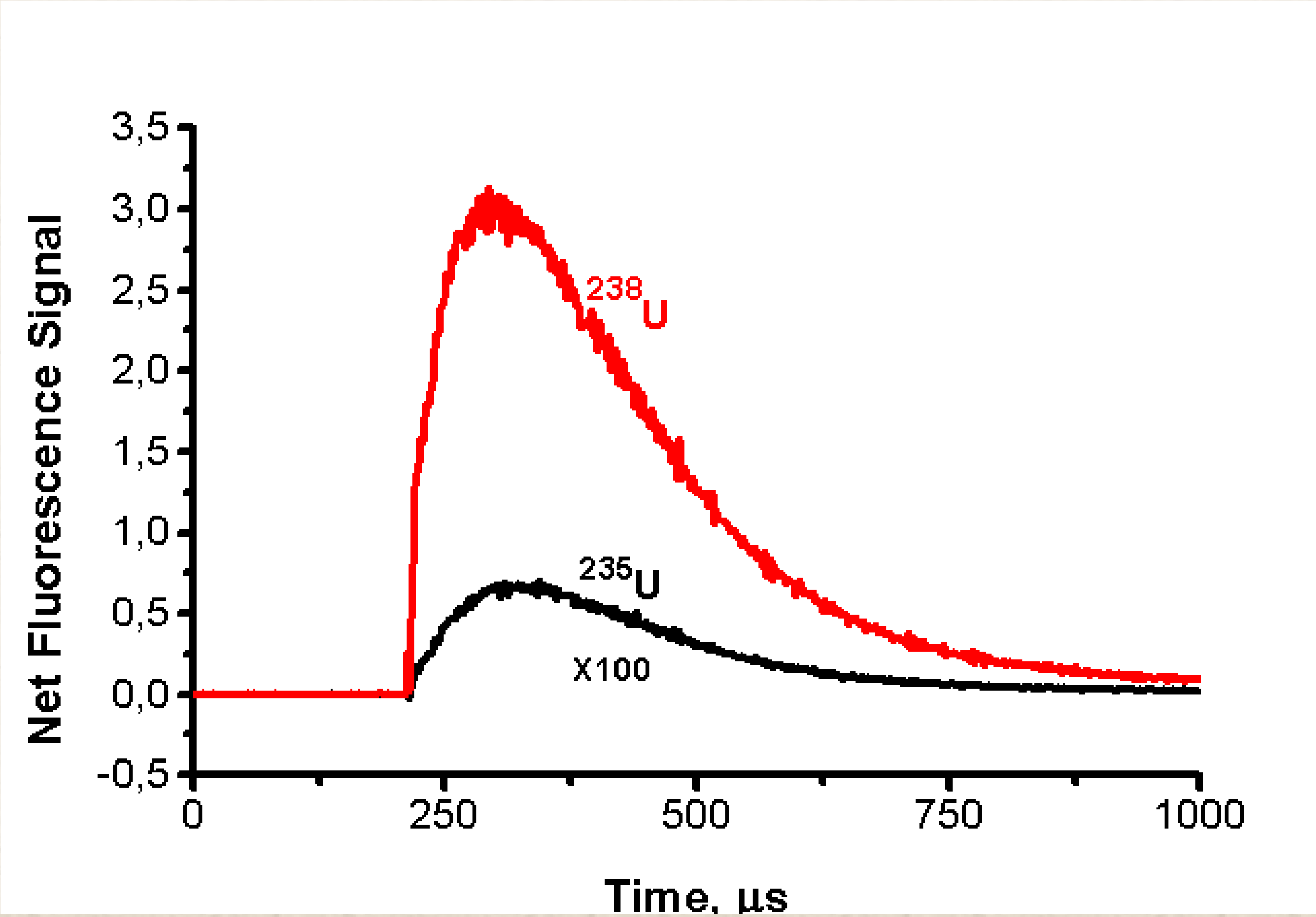
DL -- LIF. II

Time-integrating mode

DL – wavelength is fixed.

Alternative probing of the two isotopes in sequential laser shots

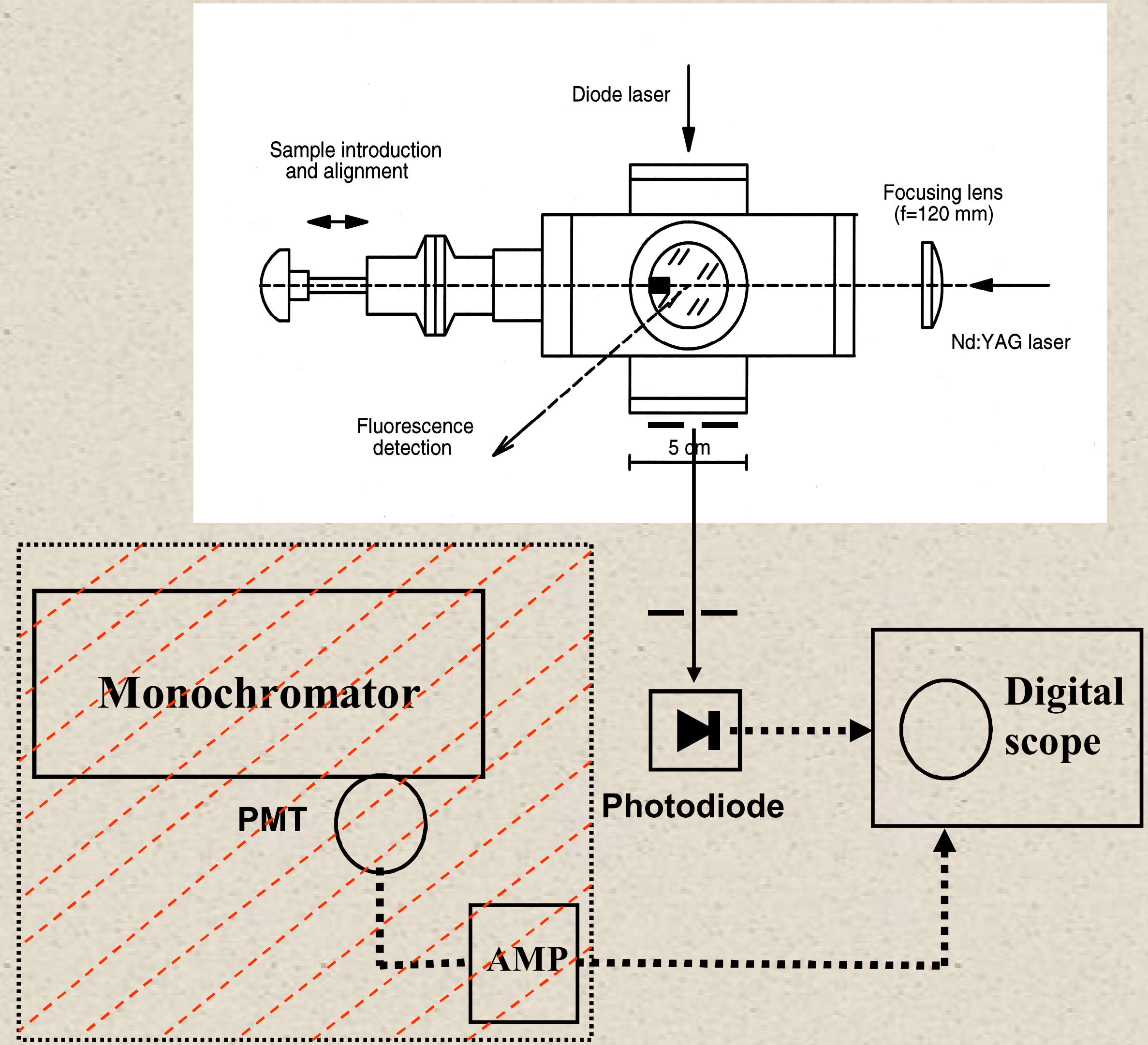
Time-dependent LIF signals of ^{235}U and ^{238}U



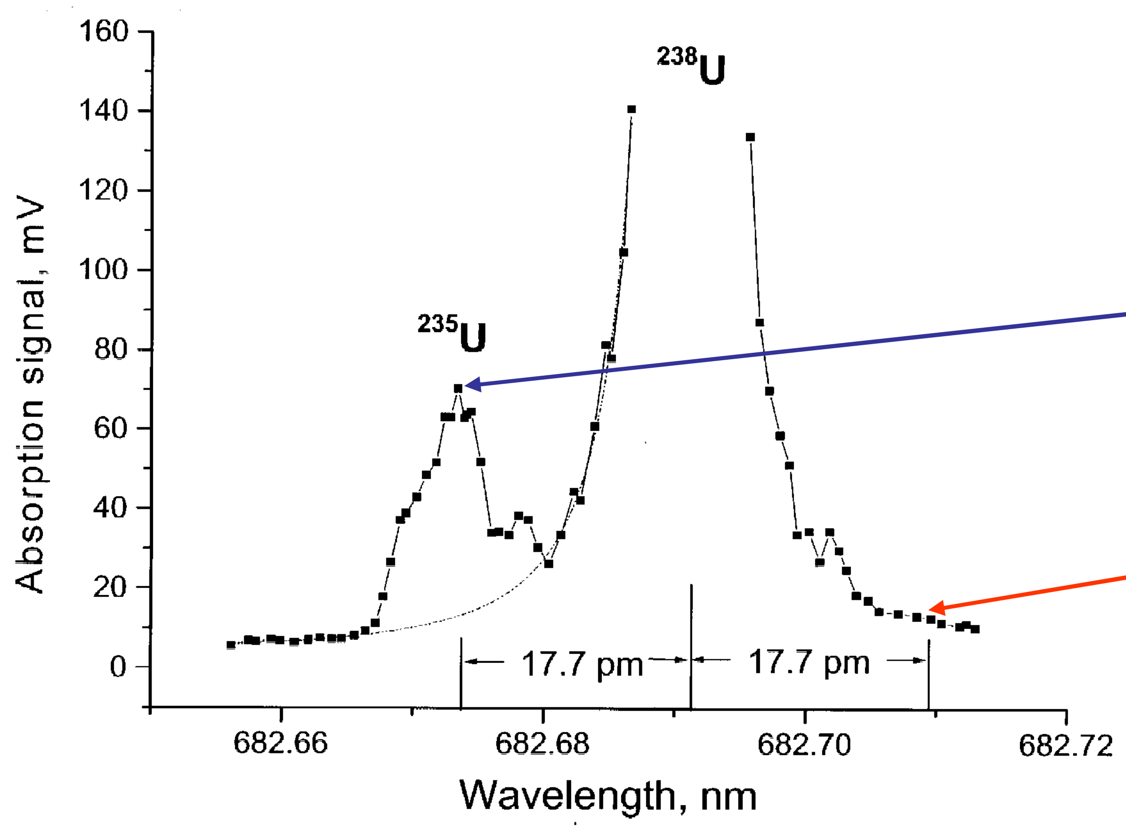
Sample of natural isotopic composition. Average of 120 ablating pulses.

DL -- AAS

Experimental set-up



Spectral profile of ^{235}U absorption line on the wing of the main ^{238}U isotope.



Net AS signal of ^{235}U =

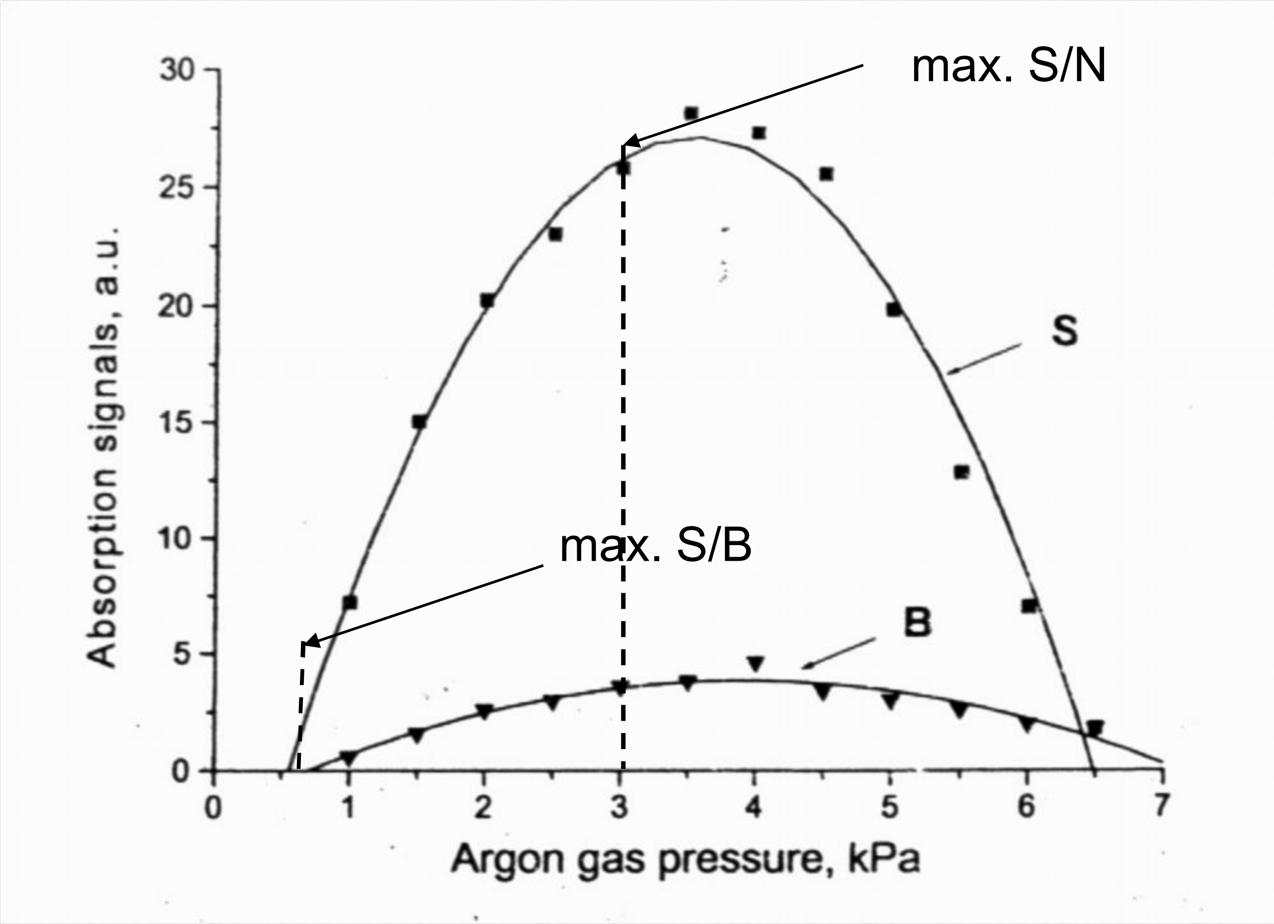
total AS signal at "blue" (-17.7 pm) wing

minus

AS signal at mirror "red" (+17.7 nm) wing

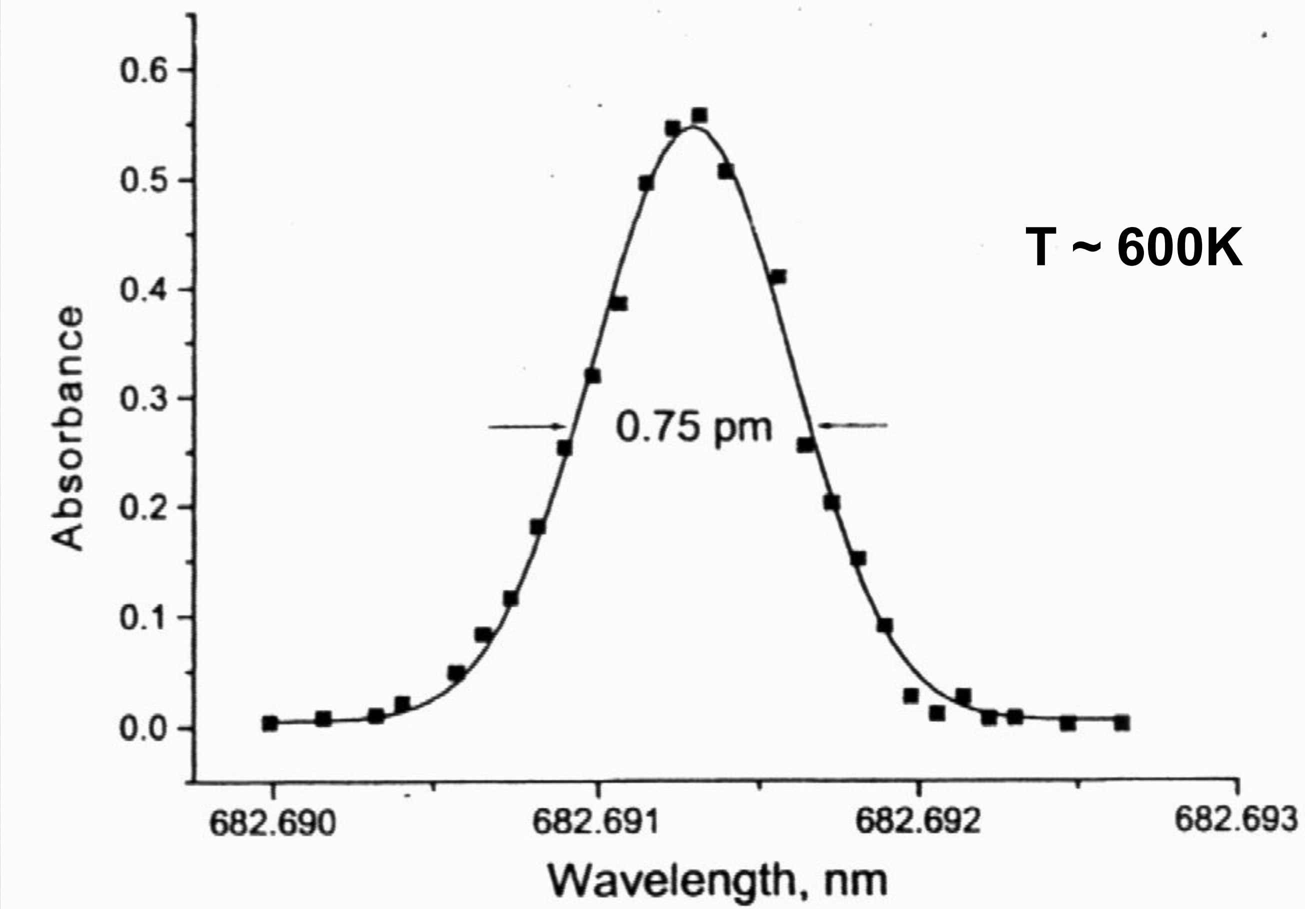
D = 5 mm, Ar pressure ~ 4 torr. The collision broadening is negligible.

Gas pressure optimization in DL-AAS



S – background corrected ^{235}U net absorption signal
B – background signal
N – background fluctuations

Doppler-limited absorption line of ^{238}U



T ~ 600K

Height 5 mm, p ~ 1 mbar, delay ~ 200 μs

Optimal experimental conditions

	DL-LIF	DL-AAS
Pressure	0.9 mbar	30 mbar
Height	8 mm	3 mm
Nd:YAG pulse energy	0.5 mJ	7.5 mJ

Analytical results

Certified conc. U^{235}(%)	Experiment (DL-LIF)	Experiment (DL-AAS)	LOD (DL-LIF)	LOD (DL-AAS)
0.714	Reference	Reference	0.6 mg/g	0.1 mg/g
0.407	0.39 ± 0.05	0.38 ± 0.02	Limiting process	
0.204	0.18 ± 0.05	0.22 ± 0.03	Plasma emission	Absorption in the wing of major isotope

Result of the determination of the $^{235}U/^{238}U$ isotope ratio by DL-AAS

Certified ^{235}U conc., (%)	Expected ratio $^{235}U/^{238}U$ (%)	Measured ratio $^{235}U/^{238}U$ (%)	RSD, (%)	Error (%)
0.714	0.719	Standard	-	-
0.407	0.409	0.38 ± 0.02	5	- 8
0.204	0.204	0.22 ± 0.03	13	9

B.W. Smith, A. Quentmeier, M. Bolshov, K. Niemax,
Measurement of uranium isotope ratios in solid samples using laser ablation and diode laser-excited atomic fluorescence spectrometry
Spectrochim. Acta B, **54**, 943 – 958, 1999

A. Quentmeier, M. Bolshov, K. Niemax,
Measurement of uranium isotope ratios in solid samples using laser ablation and diode laser atomic absorption spectrometry
Spectrochim. Acta B, **56**, 2001, 45-55

Thank you for kind attention

U^{235} line on the wing of the major isotope U^{238}