Elemental Analysis of Systems Based on Gold Nanoparticles Using of X-Ray Fluorescence and Inductively Coupled Plasma - Optical Emission Spectroscopy

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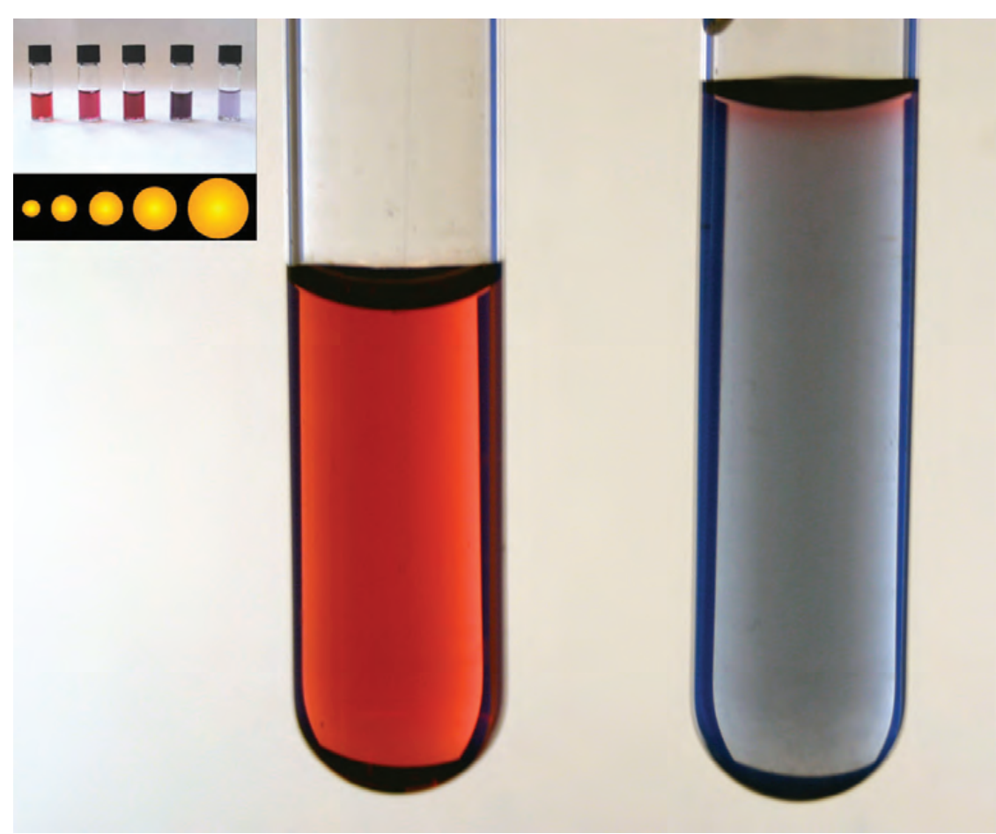
Motivation

Systems based on modified gold nanoparticles (Au NPs) has been prepared and studied thoroughly for various scientific and practical applications, e.g. in optical spectroscopic techniques, plasmonics, photonics, electronics, separation science and construction of chemical sensors. Both the final nano-particulate systems and various precursors (intermediate systems) have to be characterized by various physico-chemical methods. The information on elemental composition is crucial for the estimation of the content of nanoparticles in the systems and for calculation of their coverage by modifying (mostly organic) ligands.



Examples of gold nanoparticles

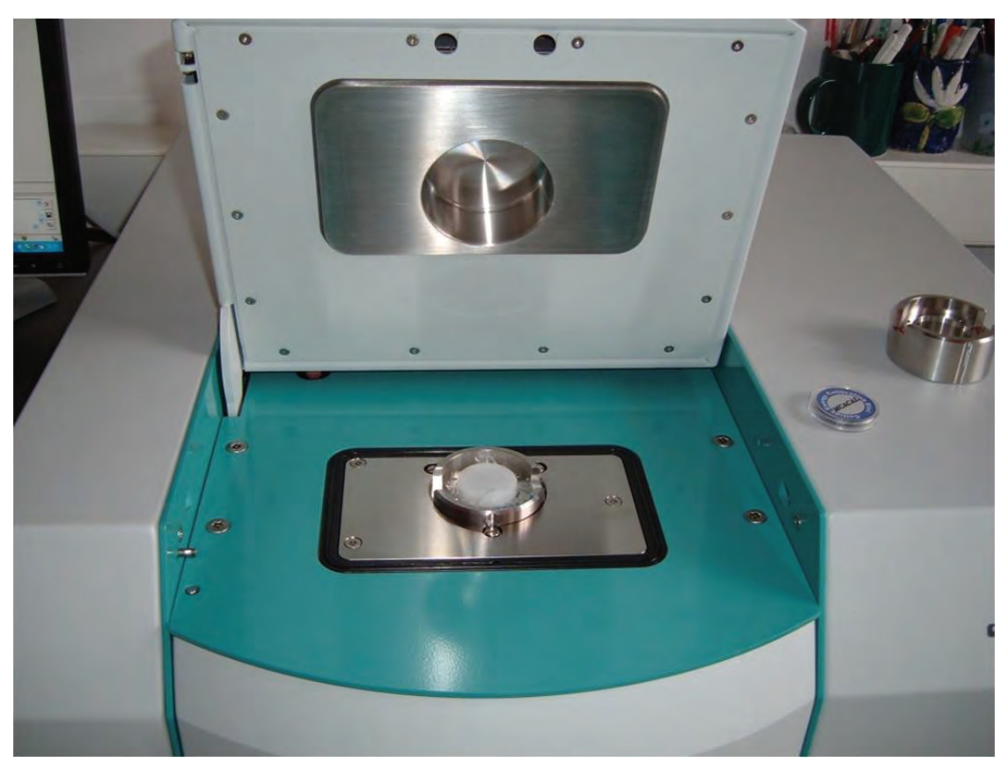
Energy dispersive X-ray fluorescence spectrometry

Energy dispersive X-ray fluorescence (ED-XRF) spectrometry is used in Analytical laboratory of IOCB predominantly for "routine" determination of various elements in newly synthesized organic compounds. The developed methodology is based on measurements of solutions of analyzed derivative in methanol (mostly), water or another appropriate solvent. ED-XRF procedures have been developed also for characterization of gold nano-particulate aqueous or organic systems aiming at monitoring of several elements, especially gold and sulfur, because thiol group is ordinarily used for fixation of organic derivatives on gold surfaces. However, the possibilities of sulfur determination by ED-XRF are very limited (it is easily possible for organic compounds before their fixation on gold), because the S K_α line is interfered by Au M lines.

Sample preparation for ED-XRF measurement: Both aqueous and methanolic systems were analyzed mostly in original (untreated) state after filling in a special liquid cell without any sample destruction. Other solvent systems (chloroform, toluene…) were firstly gently evaporated to remove disturbing organic matrix, then the samples were dissolved in 1 - 2 drops of aqua regia and water or methanol were added to achieve defined volume/weight to be transferred in the cell.

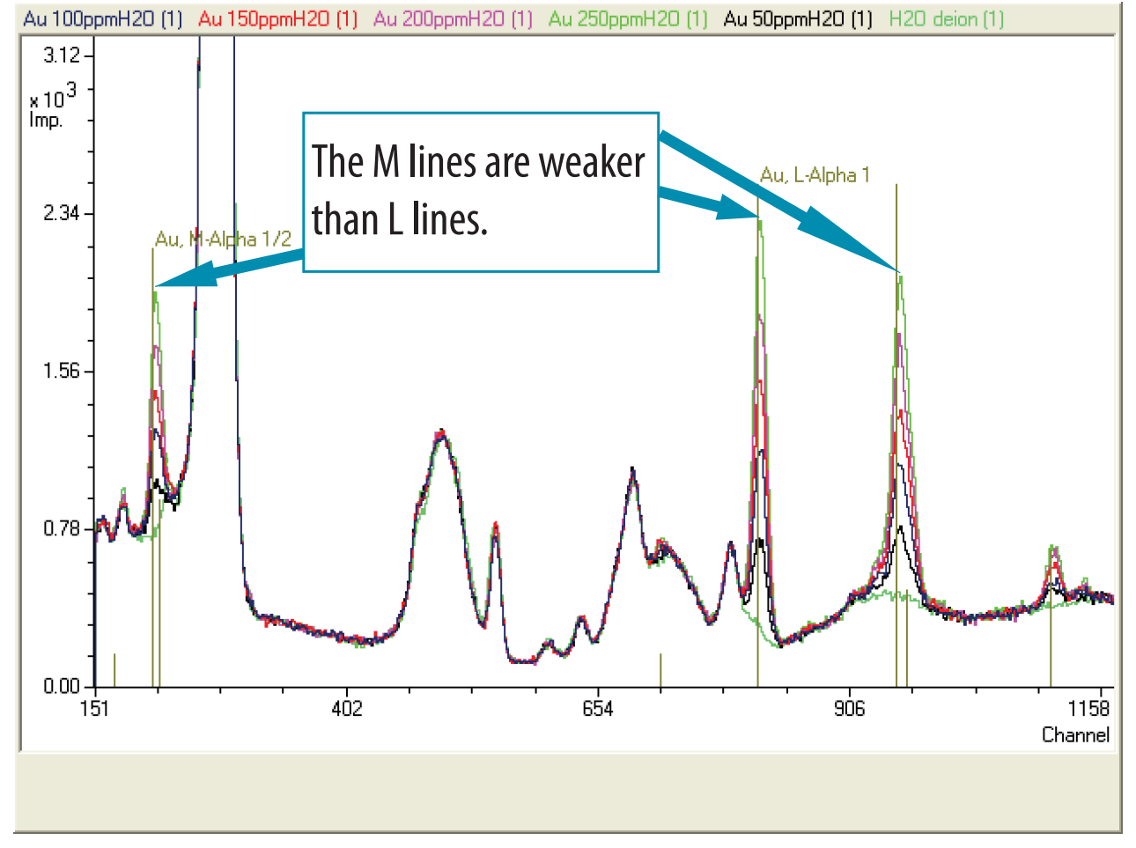
ED-XRF spectral measurements: All measurements were performed on the Spectro iQII ED-XRF spectrometer. Both the aqueous and methanolic calibration solutions were prepared using potassium dicyanoaurate(I) ($KAu(CN)_2$) and the calibrations were verified by a certified standard (purchased from Analytika, s.r.o.).

Experimental conditions: Measurement time 180 s, Voltage 48 keV, Barkla scatter, HOPG, liquid cell with 4 μm prolene foil, protection foil on sample holder 4 μm prolene.



ED-XRF spectrometer Spectro iQII

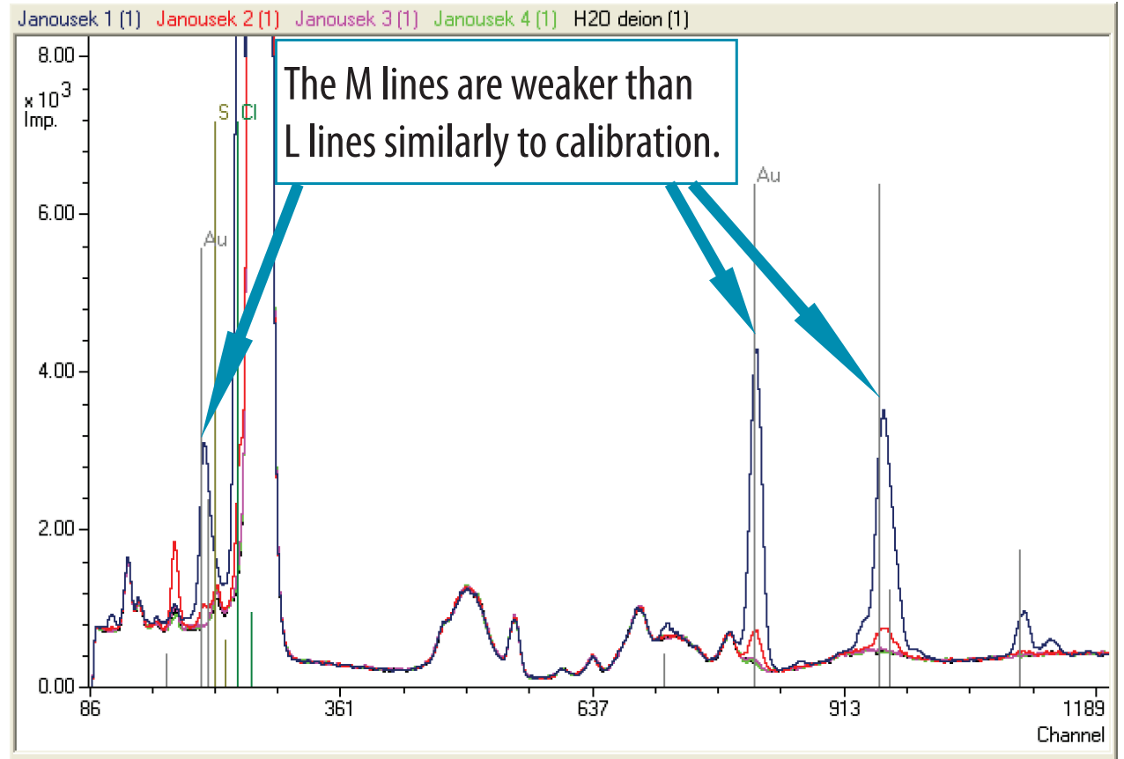
ED-XRF spectra - calibration in H_2O



The M lines are weaker than L lines.

Concentration range: 0 - 250 ppm

ED-XRF spectra - AuNPs in H_2O

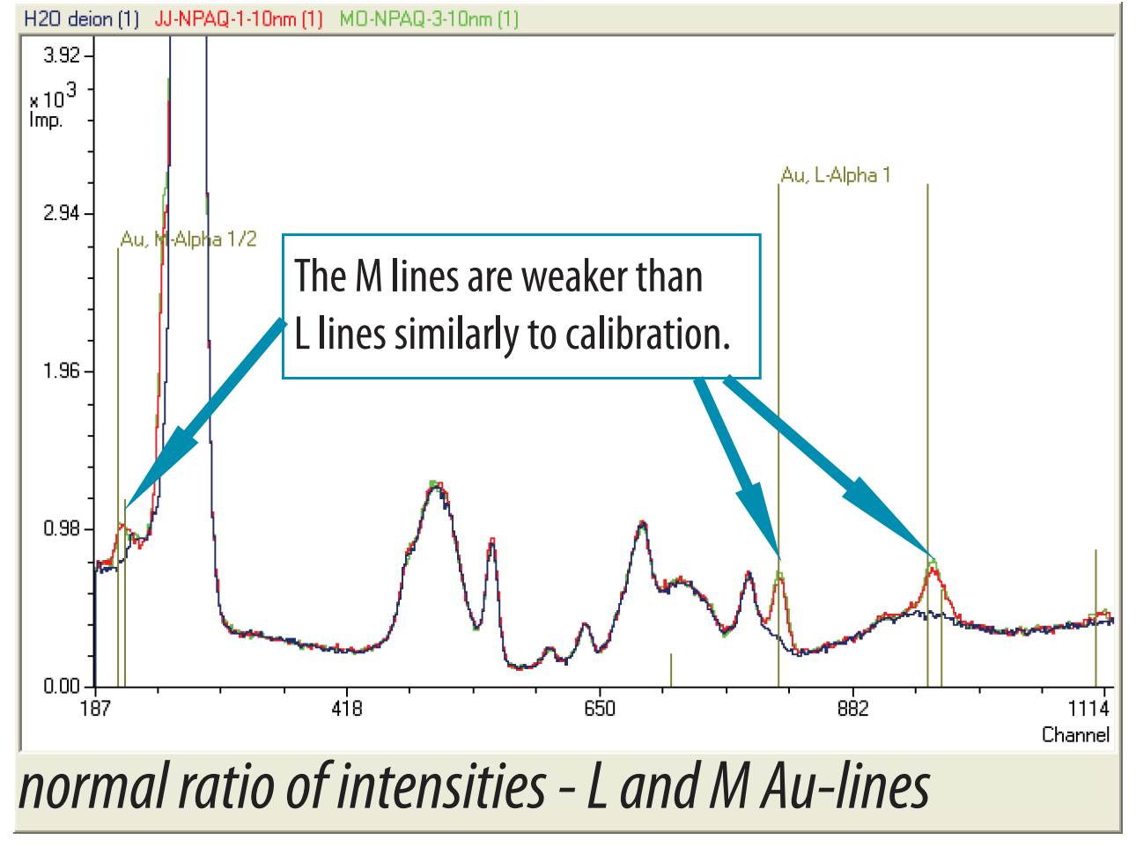


The M lines are weaker than L lines similarly to calibration.

normal ratio of intensities - L and M Au-lines

Suitable systems for quantification by ED-XRF

ED-XRF spectra - AuNPs in H_2O



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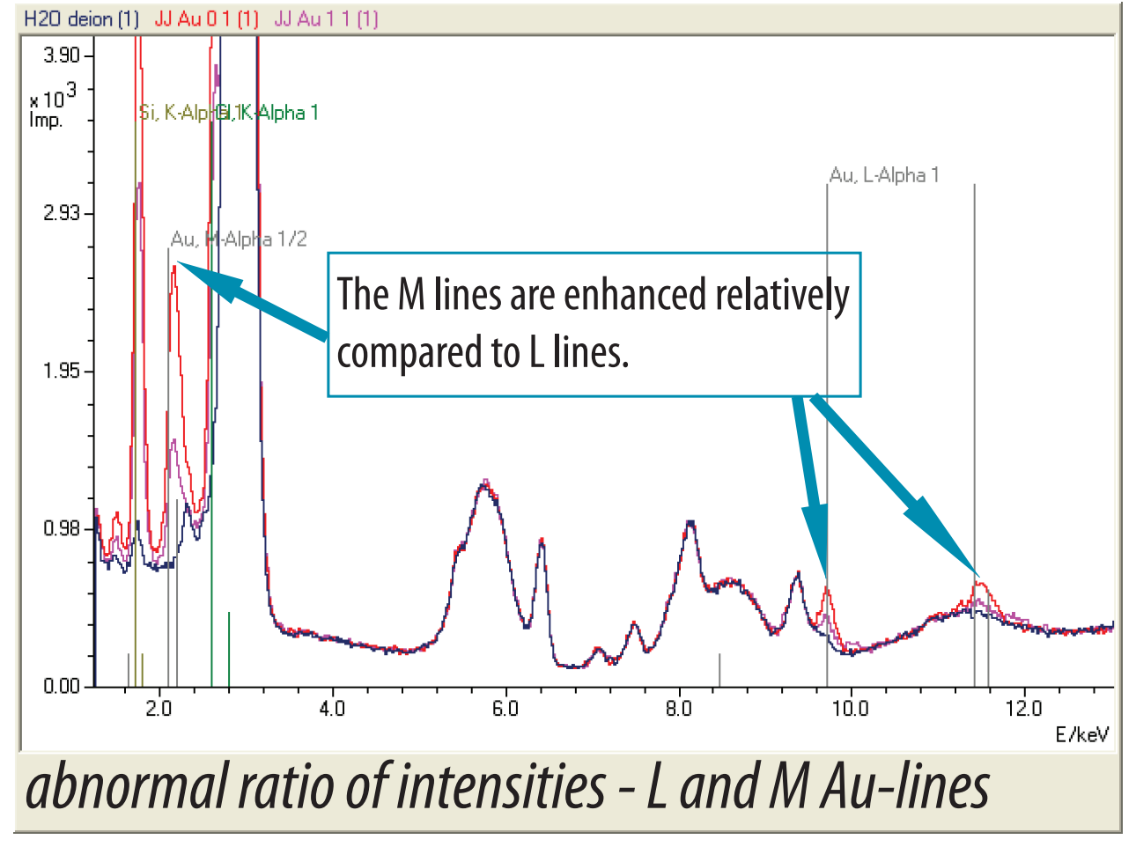
Suitable systems for quantification by ED-XRF

ED-XRF spectra - AuNPs in H_2O

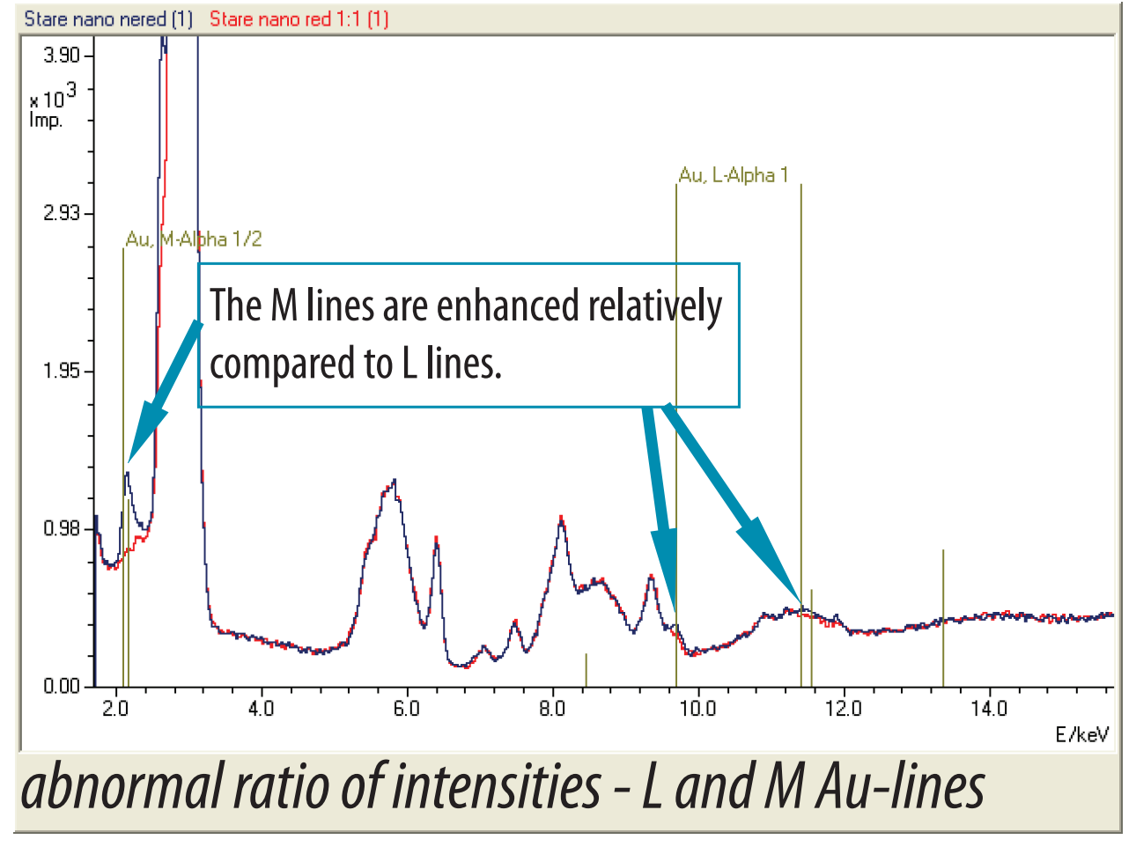


The M lines are enhanced relatively compared to L lines.

abnormal ratio of intensities - L and M Au-lines

Unsuitable systems for quantification by ED-XRF?

ED-XRF spectra - AuNPs in H_2O

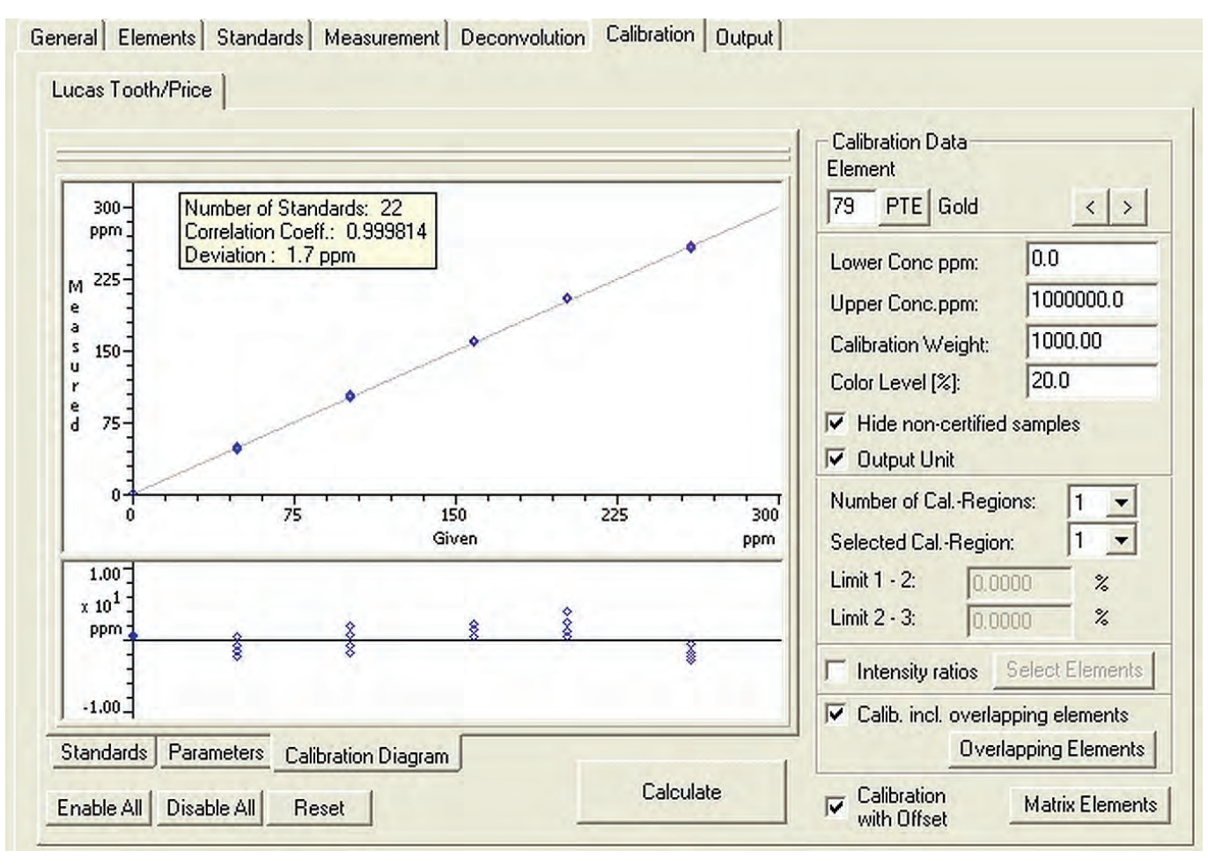


The M lines are enhanced relatively compared to L lines.

abnormal ratio of intensities - L and M Au-lines

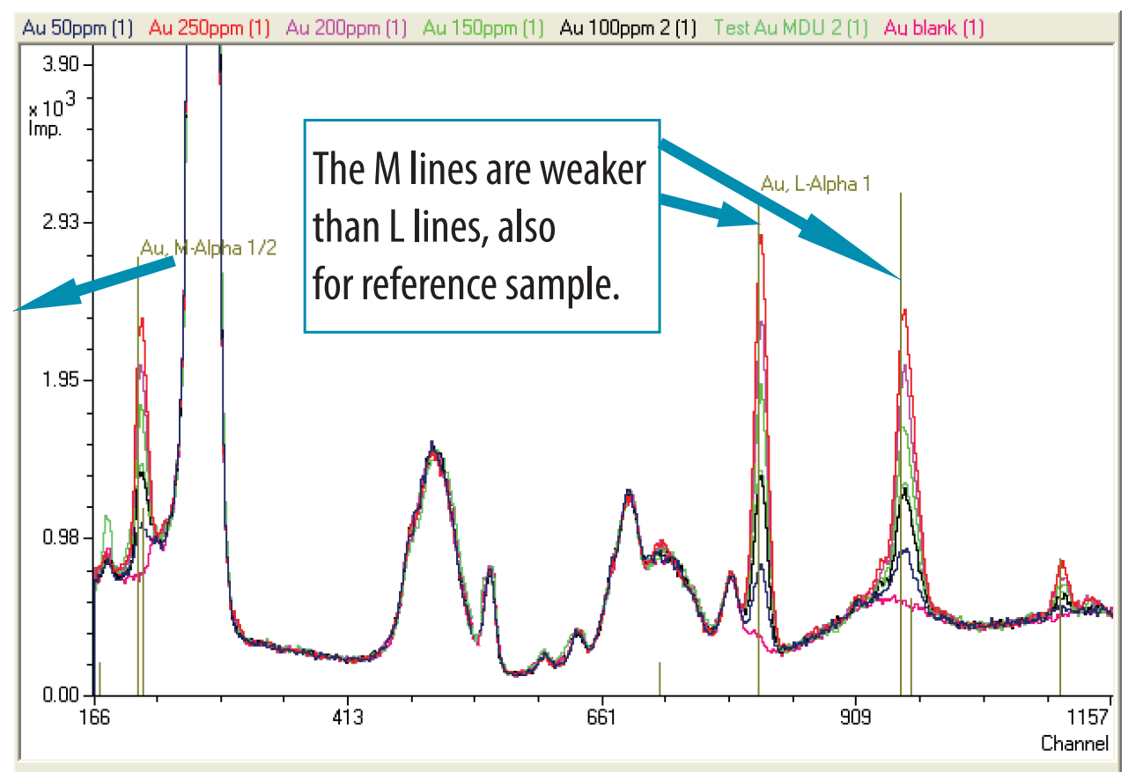
Too dilute systems for quantification by ED-XRF

ED-XRF - calibration results in MeOH



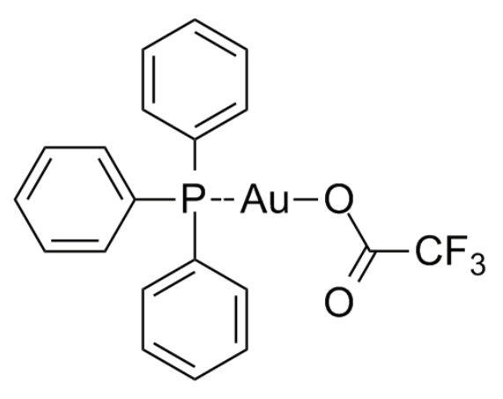
Concentration range: 0 - 250 ppm

ED-XRF spectra - calibration and reference sample in MeOH



The M lines are weaker than L lines, also for reference sample.

normal ratio of intensities - L and M Au-lines



reference sample - organically bound gold

Concentration range: 0 - 250 ppm

Problems and discussion:

1) Unusual ratios of L and M lines of gold have been observed with relative enhancement of M lines for several "native" nano-particulate systems. The issue is, if the calibration method based on intensities of Au L-lines can be used for such cases affected by the enhancement effect of Au M-lines or not?
2) The detection limits both for aqueous and methanolic systems have been estimated 4 - 5 ppm. It is insufficient for characterization of several (quite dilute) nano-particulate systems.
3) The minimal amount of final prepared sample (to be filled in the cell) for determination via our ED-XRF method is 3 g. But the available sample amount for analysis is often very low (< 1 ml) and it cannot be diluted.

Thus, we seek another method for determination of gold in AuNPs systems.

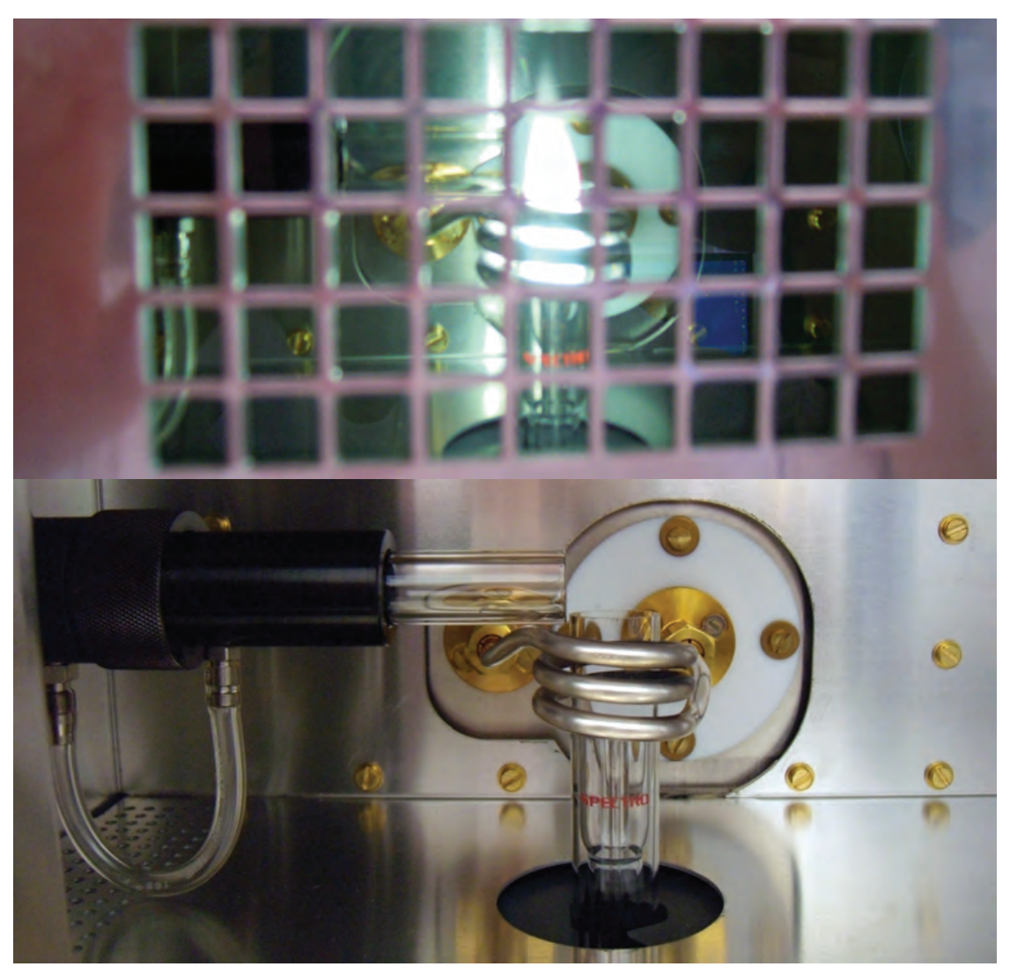
Inductively coupled plasma – optical emission spectroscopy

Inductively coupled plasma – optical emission spectroscopy (ICP-OES) is used basically as a supplementary method to ED-XRF. The determination of gold content based on ICP-OES has been developed for characterization of AuNPs systems prepared in both aqueous and various non-aqueous media.

Sample preparation for ICP-OES measurement: Two different approaches have been tested. The first one (**I**) represents dissolution of AuNPs without mineralization of organic components. Either 200 μL or 400 μL aliquot (precisely weighed) of Au NPs was transferred in a glass bottle, 0.40 mL of concentrated aqua regia was added, the system was mixed and then deionized water was added to the mass of 10 g. The second one (**II**) includes both dissolution of AuNPs and organic matrix decomposition. Firstly, either 200 μL or 400 μL aliquot (precisely weighed) of Au NPs was transferred in a glass bottle, the solvent was evaporated near to dryness, then 1 mL of conc. HNO_3 and 1 mL of H_2O_2 (30 % w/w) were added and the mixture was boiled near to dryness, then 0.5mL of HNO_3 was added and the system was boiled to dryness. After cooling to laboratory temperature, the bottle was weighed, 0.4 mL of conc. aqua regia was added, the system was mixed and sonicated for 2 min and then deionized water was added to the mass of 10 g. Both procedures were compared with standard addition method where two different additions were used corresponding to double and triple values of expected amount of Au in the sample (the procedure was without mineralization).

ICP-OES spectral measurements: All measurements were performed on the Spectro Arcos ICP-OES spectrometer with radial plasma observation.

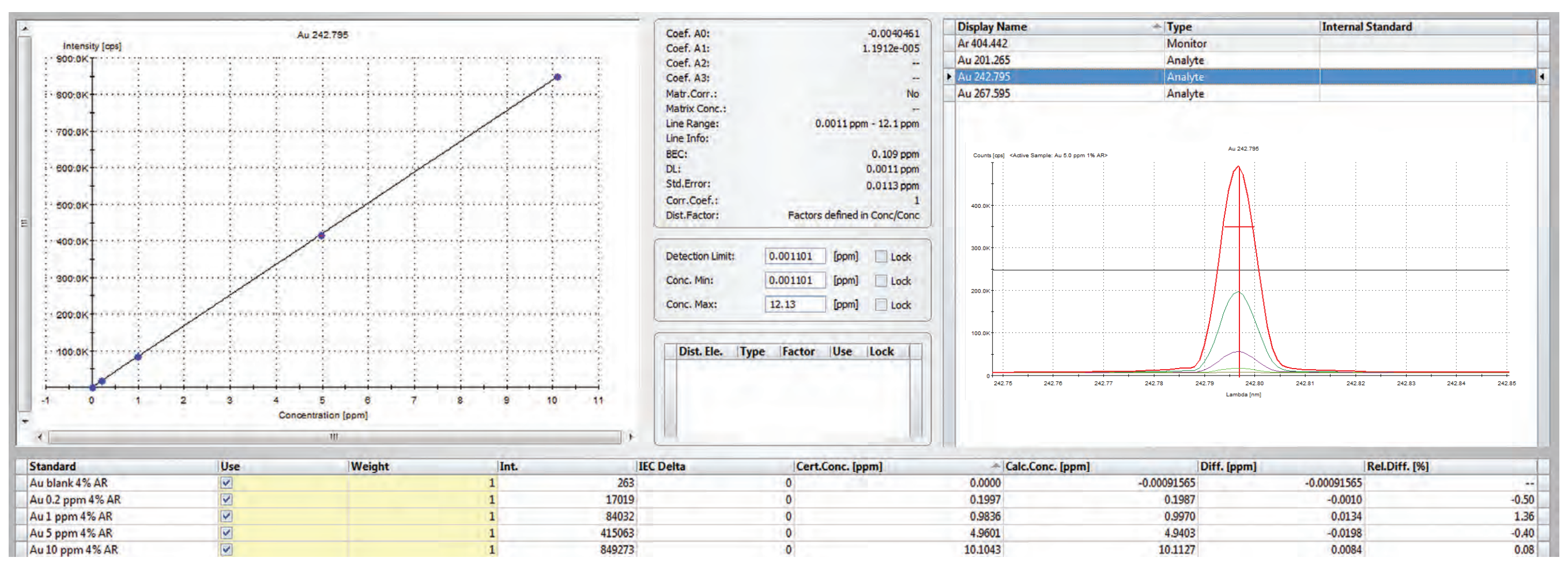
Measurement conditions: Power 1450 W, coolant flow 13 L/min, auxiliary flow 0.8 L/min, nebulizer flow 0.8 L/min, plasma torch quartz, fixed, 1.8 mm injector tube, spray chamber cyclonic, nebulizer Modified Lichte, sample aspiration rate 2.0 mL/min, 3 replicate, replicate read time 29 s per replicate, basic matrix for all measurements was 4 % (v/v) aqua regia.



Plasma torch and SOP - optical interface of Spectro Arcos ICP-OES

Potassium dicyanoaurate(I) ($KAu(CN)_2$) as a standard used for ED-XRF was analyzed by ICP-OES. The resulting value of Au content was (68.14±0.59) % which agree with theoretical value 68.37 %.

ICP-OES - calibration results



Concentration range: 0 - 10 ppm

ICP-OES - example of results of AuNPs analysis (compared to ED-XRF)

type of preparation	I				II				Std.Add.	ED-XRF
aliquot, μL	200		400		200		400		400	original system of AuNPs
	w (Au), μg/g				*w* (Au), μg/g				*w* (Au), μg/g	*w* (Au), μg/g
	59.1	59.2	61.8	60.0	56.1	53.9	56.5	55.1	61.3	63.6 58.5
	59.7	59.3	62.3	59.8	58.2	56.6	55.3	56.2	60.6	62.4 61.2
	58.5	59.9	62.0	60.5	57.3	57.1	55.5	55.6	61.3	60.7 59.7
average	**59.1**	**59.5**	**62.0**	**60.1**	**57.2**	**55.8**	**55.7**	**55.6**	**61.1**	**61.0**
SD	0.6	0.4	0.3	0.4	1.0	1.7	0.7	0.6	0.4	1.8

Notes: *All the values from ICP-OES are re-calculated to values of gold content in original AuNPs systems.*
The given values are results of independent measurements including sample preparation.

Comparison of preparation procedures:

Procedure **I** (i.e. without mineralization of organic components) is more suitable than procedure **II**. Mineralization causes probably some losses of material.

The results of procedure (**I**) are comparable with the method of standard addition. The influence of organic components seems to be negligible.

Comparison of ICP-OES and ED-XRF results:

The results of ED-XRF are comparable with the results of ICP-OES when the concentration of AuNPs is in the working range of the methodology and a sufficient amount of the sample is available. The preparation and measurement procedures are rather simpler in the case of ED-XRF than ICP-OES.

The ICP-OES technique has to be used for diluted AuNPs systems and/or in the case of low amounts of samples. The results of ICP-OES could verify the data obtained by ED-XRF.

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