VERIFICATION OF THE URANIUM MATRIX EFFECT ON SOME ANALYTES IN INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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ABSTRACT

The effect of Uranium matrix concentration on the ion signal of several concomitant elements in samples at a fixed concentration was verified. It was found that the presence of the Uranium matrix induces such a strong suppression on analyte ion signal that the count rate has dropped a factor of 1000 as the matrix concentration increased up to 0.01 mol U/l. This fact makes real Uranium analysis more complex and demands the examination of alternatives to compensate this effect.

1. INTRODUCTION

The acceptance of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) as a superior technique for multielemental and isotopic analysis has increased worldwide due to its high sensitivity, low detection limits, good linearity and excellent sample throughput [1, 2]. These are the reasons for the application of the technique in several technological fields such as the environmental, health monitoring, metallurgical and nuclear [3, 4].

In spite of these features, the existence of some severe forms of interferences [5] requires additional studies to evaluate the problems associated to the analyses of specific samples.

The purpose of this work is to assess the influence of the Uranium matrix on the ion signal of some analytes present in the Uranium solution as trace impurities.

The fact that these impurities (Be, B, Co, In, Pb, Cd, Gd and Sm) are neutrons absorbers and therefore decrease the nuclear reaction power output, means that their quantity in the reactor fuel must be strictly controlled [6].

Inductively Coupled Plasma Mass Spectrometry has proven to be one of the most powerful techniques to be applied to such analytical task [7] since its limitations are identified and assessed.

2. EXPERIMENTAL SECTION

2.1 SAMPLE PREPARATION

The solutions to be analyzed were prepared from single element stock solutions at 1000 μg/ml concentration properly diluted with deionised water and acidified for sample digestion with 65% high purity nitric acid so as to give a final solution acid concentration of 2% in volume.

Thus, a matrix free solution (blank) and 10 Uranium matrix solutions with concentration ranging from 0.0001 up to 0.1 mol U/l were prepared.

The additions of Be, B, Co, In, Pb, Cd, Gd and Sm in order to produce a final concentration of 1.0 μg/ml have enabled the monitoring of their ion signal and consequently the establishment of the desired correlation between matrix and analyte response.

2.2 INSTRUMENT SETUP

The analytical instrument used was a PLASMAQUAD PQII manufactured by VG ELEMENTAL (Cheshire, U.K.) specially prepared to handle with highly corrosive samples.

The instrument was tuned according to the instructions manual which suggests to set the operating parameters to achieve the maximum ion signal for ^{115}In contained in a calibration solution.

The solutions were pumped by a peristaltic pump (Gilson 221), the nebulizer was a De Galan type and both sampling and skimmer cones were made of Nickel.

The instrument operating parameters are summarized in Table 1.

Table 1 - Instrument Operating Parameters

ICP Parameters	**Value**
Coolant Flow Rate (l/min)	14.0
Auxiliary Flow Rate (l/min)	1.0
Nebulizer Flow Rate (l/min)	0.96
Solution Uptake (ml/min)	0.60
Forward Power (W)	1350
Reflected Power (W)	<2
Interface Parameters	
Distance from Load Coil to Aperture (mm)	10
Sampling Cone Diameter (mm)	1.0
Skimmer Cone Diameter (mm)	0.7
Data Acquisition	
Operation Mode	Peak Jumping
Points per Peak	141
DAC Step	2
Time/Sweep (s)	0.39
Dwell Time (ms)	0.32

2.3 ANALYTICAL PROCEDURE

The analytical procedure was designed to measure each analyte count rate in every solution so as to verify any possible trend as the Uranium matrix concentration increases.

The order of sample running is showed at the Table 2.

Table 2 - Order of Sample Running

Sample Number	**Matrix Concentration (mol U/l)**
1	0.0000 (blank)
2	0.0001
3	0.0002
4	0.0005
5	0.0010
6	0.0020
7	0.0050
8	0.0100
9	0.0200
10	0.0500
11	0.1000

A 120 seconds washing period was observed after each run. Indium was used as internal standard to correct the instrumental drift.

3. EXPERIMENTAL RESULTS

The results shown in Figure 1 to 8, where the analyte count rate is plotted versus Uranium concentration, reveals a progressive ion signal loss.

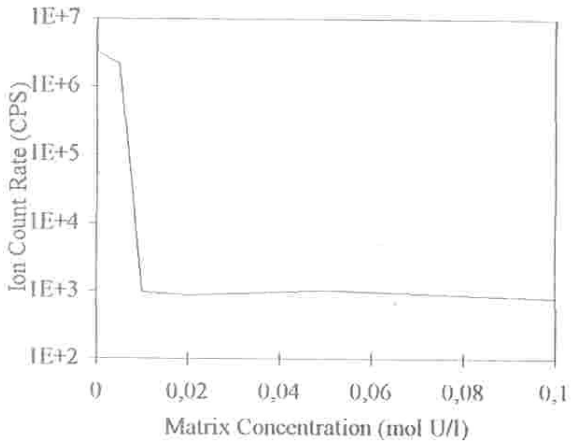

Figure 1 - Beryllium Count Rate Suppression

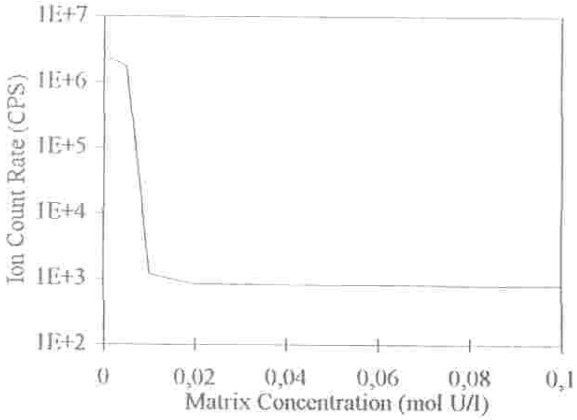

Figure 2 - Boron Count Rate Suppression

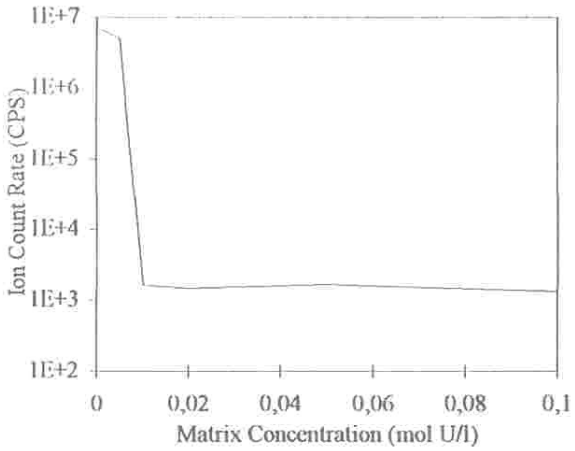

Figure 3 - Cobalt Count Rate Suppression

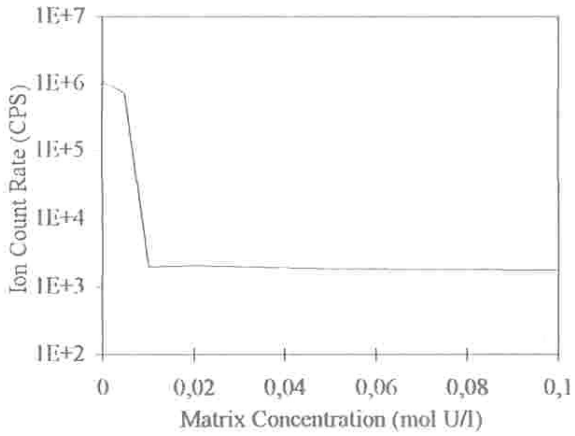

Figure 4 - Cadmium Count Rate Suppression

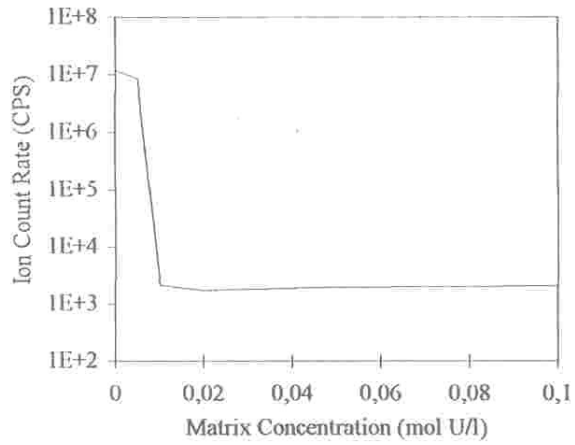

Figure 5 - Indium Count Rate Suppression

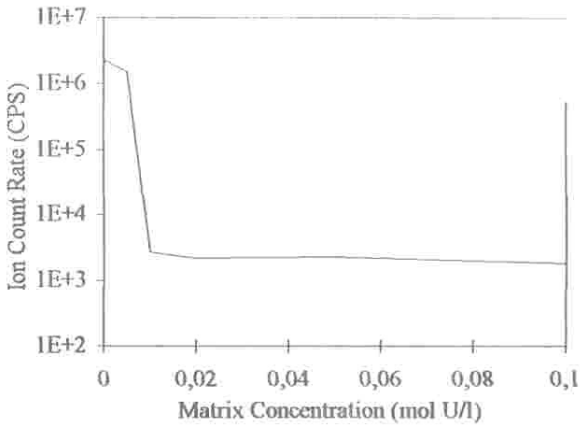

Figure 6 - Samarium Count Rate Suppression

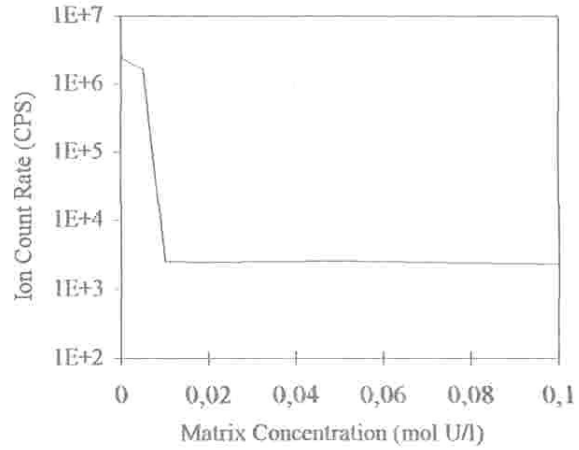

Figure 7 - Gadolinium Count Rate Suppression

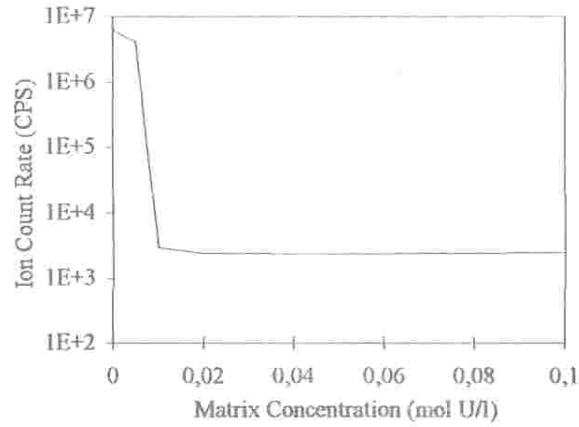

Figure 8 - Lead Count Rate Suppression

The count rate decreases linearly with the concentration from 0.0001 to 0.005 mol U/l. From 0.01 mol U/l on it remains constant with very few variations, as can be seen in Table 3 and Table 4.

Table 3 - Ion Count Rate Measured for each Sample

Matrix	Count Rate (Counts Per Second - CPS)							
(mol/l)	Be	B	Co	Cd	In	Sm	Gd	Pb
0	4006320	3142050	9096630	1138070	13046500	2561790	2456570	5688400
0,0001	3734850	2853430	7933230	1089730	11410200	2465600	2473840	6057240
0,0002	3304690	2529440	6785800	997200	11954800	2096590	2564800	6391070
0,0005	3128220	2443990	6850490	996473	11648500	2212460	2301940	5923170
0,001	2964350	2341960	6760190	977958	11060200	2199910	2250230	5707620
0,002	2697810	2180090	6318010	951983	10396600	1941820	2049360	5186050
0,005	2119570	1729490	5081620	708005	8599370	1570640	1674780	4125350
0,01	980,91	1196,1	1612,9	1963,2	2124,3	2730,9	2524,4	2991,5
0,02	893,05	845,72	1457	2046,3	1764,9	2158,3	2475,2	2457,6
0,05	1039,5	815,69	1644,1	1859,3	1976,3	2253,8	2573,7	2401,3
0,1	805,18	805,68	1316,8	1755,4	2060,9	1824,4	2302,7	2513,8

Table 4 - Ion Count Rate Suppression Percentage for each Sample

Matrix	Be	B	Co	Cd	In	Sm	Gd	Pb
(mol/l)	%	%	%	%	%	%	%	%
0	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
0,0001	6,78	9,19	12,79	4,25	12,54	3,75	-0,70	-6,48
0,0002	17,51	19,50	25,40	12,38	8,37	18,16	-4,41	-12,35
0,0005	21,92	22,22	24,69	12,44	10,72	13,64	6,29	-4,13
0,001	26,01	25,46	25,68	14,07	15,22	14,13	8,40	-0,34
0,002	32,66	30,62	30,55	16,35	20,31	24,20	16,58	8,83
0,005	47,09	44,96	44,14	37,79	34,09	38,69	31,82	27,48
0,01	99,98	99,96	99,98	99,83	99,98	99,89	99,90	99,95
0,02	99,98	99,97	99,98	99,82	99,99	99,92	99,90	99,96
0,05	99,97	99,97	99,98	99,84	99,98	99,91	99,90	99,96
0,1	99,98	99,97	99,99	99,85	99,98	99,93	99,91	99,96

The ion signal loss percentage shown in Figure 9 suggests that there is a correlation between suppression and analyte atomic mass unit. In fact, lighter elements like ^{9}Be, ^{11}B and ^{59}Co were more suppressed than ^{112}Cd, ^{151}Sm, ^{157}Gd and ^{208}Pb.

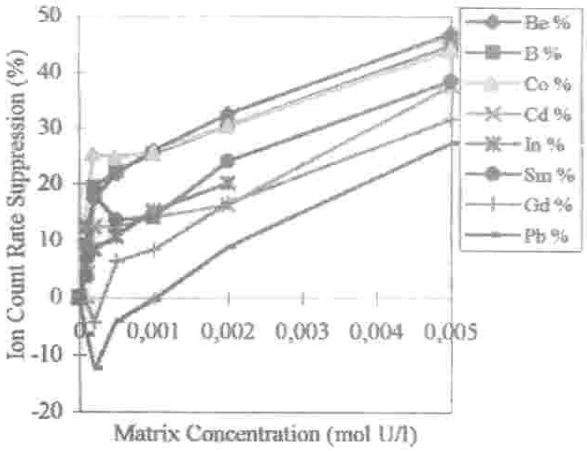

Figure 9 - Matrix Suppression

The observation of the first ionization energy for the elements investigated here and summarized at Table 5 suggests that there in another correlation between the analyte degree of ionization and suppression. It is clear that the Be, B, Co and Cd with first ionization energies above 7.8 eV are more suppressed than Sm, Gd and Pb which have values below 7.4 eV.

Table 5 - First Ionization Energies for some Elements

Element	First Ionization Energy
(m/z)	(eV)
^{9}Be	9.32
^{11}B	8.30
^{59}Co	7.86
^{112}Cd	8.99
^{115}In	5.79
^{151}Sm	5.63
^{157}Gd	6.14
^{208}Pb	7.42
^{238}U	6.08

Both correlations confirm the general rule stated by Gregoire elsewhere [8]:
"... the lower the atomic mass of the analyte and the lower the degree of ionization of the analyte in the plasma, the greater will be the effect of a given matrix element on the ion count rate of the analyte. For a given analyte, the greater the atomic mass of the added element and the greater the degree of ionization of the added element in the plasma, the greater will be the effect of the added element on the analyte ion count rate."

Several theories were developed by different authors to explain the mechanism of this interference: a) shift in ionization equilibrium, b) volatilization or lateral diffusion effects, c) collisional process and ambipolar diffusion. Each one seems to be adequate to explain a particular set of experiments but is not able to be confirmed throughout. Much has to be done here.

4. CONCLUSION

It is evident from the experimental data the harsh suppression produced by the Uranium matrix on the analyte ion signal.

The fact that at just 0.01 mol/l the analyte ion signal has dropped nearly 100% of its original value is a clear indication that a direct quantitative analysis would not be reliable and some alternative must be searched to compensate the matrix effect.

There are five classical solutions reported in literature [10]: a) matrix matched standards, b) standard addition, c) isotopic dilution, d) dilution of the sample and e) extraction of the matrix. A balance of their advantages and disadvantages are far beyond the aim of theirs article, yet is essential to those wanting to run real Uranium samples.

5. REFERENCES

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