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COMBINED APPROACH TO ELEMENTAL HAIR ANALYSIS BY ICP-AES AND ICP-MS

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ABSTRACT: We have applied the combined approach to the routine elemental analysis of biological, pharmaceutical, nutriceutical objects as well as fresh and waste waters using the complex ICP-OES + ICP-MS for both major and trace element groups. Matrix elements (up to 15–20), such as Na, Mg, Al, Si, P, K, Ca, Fe, Zn in biological samples can be determined by ICP-OES while the rest elements except of H, C, O, F, Cl measured by more powerful ICP-MS method, which is able to quantify up to 50–60 elements, depending on element/isotope abundances. The application of two methods provides more flexibility when working with unknown matrices and provides cross-checking to improve data reliability and also enhances sample throughput.

Introduction

Elemental analysis of various clinical objects is now widely used for the diagnostics and prevention of the element imbalance related diseases. Analysis of urine, whole and prepared blood, hair and nails is of the most common use for this purpose. ICP-OES analysis and diagnostics by the element pattern in hair has been applied routinely in early 1970's, then first commercial ICP-OES systems became available. Since then, the number of elements of interest tends to increase as new understanding of the role of elements in human health is propagated. From the other side, the range is limited by the availability of the appropriate analytical instrumentation, which should be rapid, multielemental, sensitive and rather inexpensive. With the invention of ICP-MS with detection limits by 10^2–10^4 lower then those for ICP-OES and possibility to determine isotopic composition of the element, routine elemental analysis became concerned with elements normally found in samples at 10^{-9} – 10^{-12}. Clinical application of ICP-MS gave rise to a large number of investigations on elemental migration in biosphere, their importance in various biochemical processes in human.

At present, ICP-MS gives to an analyst the possibility to measure almost all elements that can be of interest in clinical, nurticeutical and pharmaceutical applications, thus becoming the most versatile elemental analyzer. However, the cost per sample analyzed by ICP-MS is rather high due to the primary cost of ICP-MS instrumentation and costs of maintenance. Taking in consideration that only a part of clinical and biological samples demand the analysis at the top of performance of ICP-MS in terms of sensitivity and element coverage, it is considerable in many cases to use the combination of ICP-OES and ICP-MS. Detection limits of ICP-OES allow the quantitative determination of at least 15 essential and toxic elements commonly occurred in concentrations >0.1–1 ppm in sample with dilution factors varying from n for body fluids to n*100 for food, drugs, hair and teeth. This range usually includes Na, Mg, Al, Si, P, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Ba, Pb. For other important elements, such as Li, Be, B, V, Co, As, Se, Rb, Cd, Sn, I, Cs, Hg, Tl ICP-OES analysis may not give adequate results. Instead, the ICP-MS analysis for latter and part of former element group may be applied.

Materials and methods

In this study the ICP-OES instrument Optima 2000 DV, PerkinElmer Inc., and ICP-MS Elan 9000, PerkinElmer Sciex Corp. were used for elemental analysis of various samples. The sample digestion procedures were performed using microwave digestion system Multiwave 3000, PerkinElmer – A. Paar.

Results

Generally, 100 mg of sample were digested in 5 ml of concentric nitric acid and diluted with deionized water to 100 ml. Matrix elements (up to 10–15), such as Na, Mg, Al, Si, P, K, Ca, Fe, Zn in biological samples were determined by ICP-OES. Usually, Mg, Sr and Pb were analyzed with both ICP-OES and ICP-MS and used for the cross check of the methods' agreement for low,

Table 1. Spike recoveries for 27 routinely measured elements in clinical and biological samples.

Element	Found in unspiked sample, ppb	Added spike concentration, ppb	Found in spiked sample, ppb	Recovery, %
ICP-MS, Elan 9000				
Li	0.0325	0.02	0.0514	94.8
Be	0.0310	0.02	0.0498	94.2
Mg	326.9	398	717.2	98.0
Ti	2.89	4.0	7.21	107.9
V	0.308	1.0	1.38	107.3
Cr	5.65	4.0	9.78	103.2
Mn	8.76	15.7	24.7	101.5
Co	0.373	4.0	4.32	98.8
Ni	6.46	23.7	28.8	93.9
Cu	80.89	4.0	85.15	106.4
As	4.02	4.0	8.05	100.7
Se	2.39	1.0	3.49	110.6
Sr	15.59	15.8	31.11	98.2
Mo	1.18	1.0	2.22	103.4
Cd	0.286	4.0	4.21	97.9
Sn	1.32	1.0	2.41	109.7
Hg	5.01	1.0	5.97	95.6
Pb	28.30	23.6	49.67	90.4
ICP-OES, Optima 2000DV				
Zn	682.1	396	1083	101.0
P	513.8	436	974.7	105.6
Fe	214.8	150	377.4	102.0
Si	17.59	48.9	65.22	97.4
Mg	346.5	398	734.1	97.3
Al	29.20	78	104.66	96.7
Ca	3101	795	3932	104.4
Na	1044	1350	2423	102.2
K	14.34	787	760.9	94.8

intermediate, and high mass ranges respectively, although this role can be assigned to any element, depending on the sample composition. ICP-MS analysis was then performed covering all elements except of high intensity signals from matrix pieces (Na, Ca, K, Fe). Both batches of results were then combined using spreadsheets. The detailed study of the proposed combined approach with spiked sample analysis showed good recoveries in the range 90–110 % for 27 studied elements, Table 1. The ICP-MS vs. ICP-OES plots for Mg, Sr and Pb, ($n > 300$) showed correlation coefficients between 0.95 to 0.99, with the slope and intercept coefficients near about 1 and 0 respectively, Figure 1-3. These values were calculated without applying internal standardization to the measured data. Therefore the use of complicated internal standardization technique for routine high throughput analysis becomes less necessary, as for the most part of biological and clinical applications the precision in the range of 90 – 110 % is quite acceptable.

Conclusion

Combination of two instruments is cost-effective and time-saving way where determination of practically all elements of interest is needed in various combinations and large scale of concentrations. The cross-check between ICP-OES and ICP-MS values ensures the reliability of measured data. Also, it becomes pos-

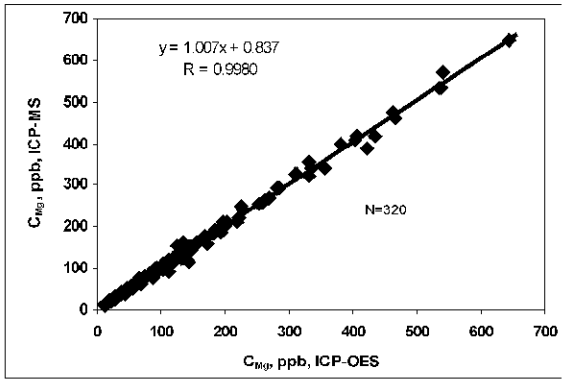

Figure 1. ICP-OES (279.077 nm) vs. ICP-MS (^{25}Mg) plot for Mg.

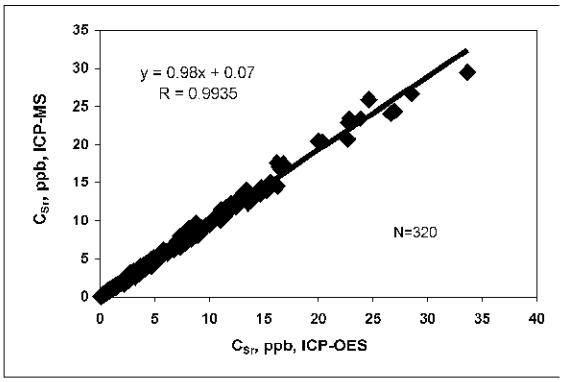

Figure 2. ICP-OES (421.552 nm) vs. ICP-MS (^{88}Sr) plot for Sr.

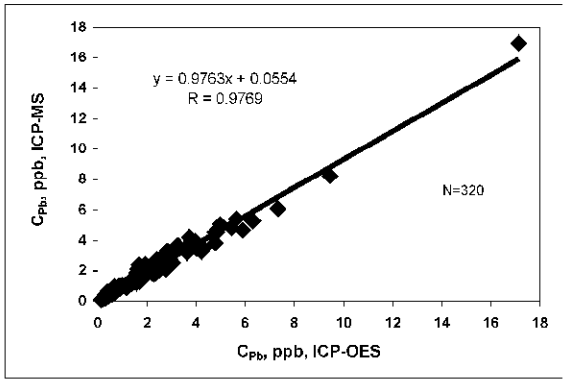

Figure 3. ICP-OES (220.353) vs. ICP-MS (^{204}Pb) plot for Pb.

sible to sort the samples by matrix type and total dissolved solids content that helps in optimizing ICP-MS analysis sequence. The life-time of ICP-MS detection system is increased as high intensity signals from matrix elements are not registered.