

Developments in Analytical Technology

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ABSTRACT

Developments made in ICP-OES and ICP-MS analytical technology over the last ten years are reviewed, focusing primarily on advancements that have impacted procedures widely available from commercial geochemical laboratories. Examples of this are the increasingly reliability of ICP-MS instrumentation that now makes it a standard production instrument providing trace analysis close to or at crustal abundance for most elements. The other significant change is the development of echelle grating solid-state detector ICP emission instruments. The high resolution offered by the echelle grating coupled with the full range of element selection and wavelength choices have dramatically improved accuracy and reduced costs. Development in ICP mass spectrometry are reviewed, the most notable development being the wider application of high resolution ICP mass spectrometry. A magnetic sector mass spectrometer is used either with an electron multiplier detector or with individual mass collectors. The magnetic sector has improved resolution by several orders of magnitude allowing accurate determinations of elements like Li, Bi, K, Cl, Fe, As, Se, Au, etc at low levels and in difficult matrices. Mass throughput is superior to quadrupole detectors so that detection limits are improved enabling highly sensitive analysis of vegetation and waters for exploration. Multi-collector technology allows for isotopic analyses that are comparable to those from thermal ionization mass spectrometry (TIMS). Sample introduction devices such as laser ablation can be used for direct analysis of solids and to determine composition of mineral grains and inclusions. In this area, MC-ICP-MS can provide superior results to TIMS.

INTRODUCTION

A superficial review of journal articles from the Journal of Exploration Geochemistry in 1997 and with those in 2007 in Geochemistry: Exploration, Environment, Analysis would seem to show an apparent lack of development in analytical technology. Papers cover projects where samples are analyzed by inductively coupled plasma – optical emission spectroscopy (ICP-OES), inductively coupled plasma – mass spectrometry (ICP-MS), x-ray fluorescence (XRF) and instrumental neutron activation analysis (INAA) for multi-element analyses to aid in the interpretation of geochemical signatures, deposit formation, methods for detecting new exploration targets. Similarly, comparison of a commercial fee schedule from 1997 with one from 2007 would also appear to indicate few if any strikingly new developments. Commercial laboratories in 1997 were offering multi-element packages, selective leaches, hydrochemistry and rare earth determinations using ICP-MS. A look below the surface though does show some real changes.

A paper by Prendergast (2007) is representative of the changes that have occurred. The paper describes a multi-element exploration program involving 1500 samples and determination of 36 elements by a combination of ICP-MS and ICP-OES. The detection limits from the procedure were evaluated and found to adequately encompass the observed

backgrounds of samples from previous studies. The range of major, minor and trace elements enabled both the characterization of altered and enriched samples plus that of lithological and stratigraphic domains. All of this information from one analytical package from a commercial laboratory at a cost that made the analysis of all samples a reasonable prospect during the exploration program. While the articles from 1997 described multi-element determinations, they were rarely applied to as many samples, or for such a range of elements; in addition numerous elements were often below method detection limits.

MULTI-ELEMENT ANALYSIS – FULL ELEMENTAL COVERAGE FROM CRUSTAL ABUNDANCE TO ORE GRADE LEVELS

The above study utilizes the kind of commercial package that come to be widely available in the last ten years and is used throughout the industry for exploration and other studies. Following either an aqua regia digestion, a stronger digestion using perchloric and hydrofluoric acid or a fusion, forty to fifty elements, including major, minors and traces are reported using a combination of ICP-OES and ICP-MS. While multi-element packages were commercially available in the mid nineties, further evolution and adaptation of instrumentation and

laboratory procedures has only continued to improve these packages. It is not uncommon to have package reporting 50 plus elements at detection limits at or below crustal abundance for virtually every element. A perchloric/ HF digestion package from 1998 reported 40 elements by ICP-OES. Now the comparable package reports 50 plus elements with 17 at lower detection limits for the same price in inflation adjusted dollars. This kind of survey tool is changing routine exploration, downhole geochemistry and research.

Analysis of geochemical samples presents some real challenges. The range of concentrations in geochemical analysis that needs to be addressed is wide. Major elements are present at percent levels. Trace elements such as Se and Te have crustal abundances at the sub-part per million (ppm) level and to be determined adequately require the sensitivity of ICP-MS. Important trace element indicator elements such as arsenic can range from a few ppm to hundreds of ppm. Levels of other elements may cover wide ranges: Cu at sub-ppm levels in a selective leach, ten's of ppm in grass roots exploration and percent levels for on-site and target drilling.

There have been some instrumentation developments that have helped laboratories meet these wide dynamic range requirements, with suitable quality for exploration and at pricing that can fit into exploration budgets.

ICP Emission Instrumentation – Echelle Gratings and Solid-State Detectors

The first technological advance to be considered is the development and then wide adoption of echelle grating optical systems solid state detectors for ICP-OES. Two papers by Barnard et al. (1993a, 1993b) describe this work for the manufacturer Perkin Elmer. At the same time, other instrument manufacturers were developing similar instrumentation. By the late 90's, most commercial geochemical laboratories had replaced older photomultiplier tube instruments with solid state detector echelle based instruments for all their large multi-element packages. Echelle spectrometers bring high spectral resolution and reduce interferences from spectral overlap. Solid state type detectors offer high flexibility in the choice of emission lines and can monitor spectral backgrounds simultaneously. These detector arrangements also allowed for the simultaneous determination of all other elements of interest along with backgrounds during one reading.

Beyond backgrounds and multiple elements, echelle based solid-state detector systems also allowed, for the same amount of analysis time, the determination of multiple elements and multiple emission lines for each element. This has provided tremendous flexibility in managing elements with large ranges of concentrations. Zinc determinations can be done by using two emission lines, one sensitive for trace concentrations and one less sensitive for higher grades. Similarly, the calibration for major elements such as Fe, Al and Ca can be extended to cover 100 ppm to > 50% through the use of multiple lines.

Echelle gratings' increased resolution eliminated many spectral overlaps that had been problematic in the past. For cases where there are still issues, the flexibility of line selection can improve accuracy. In the case of bismuth, the most sensitive

line has high Cu line interference. The alternative bismuth line has a detection limit that is higher by a factor of five but when high concentrations of copper are present in the sample it is a better choice. At the data reporting stage, the choice of which line to report can be based on the Cu concentration for each individual sample.

ICP Emission – Radial versus Axial Viewing

Most commercial laboratories used radially viewed ICP-OES systems which offered a large element selection, wider dynamic ranges and higher resolution to reduce interferences. What they did not offer was lower detection limits. Axial viewing of the ICP plasma, looking down the plasma, rather than at its side, does offer lower detection limits. By the mid-nineties, most ICP emission manufacturers were offering versions of instruments capable of axial viewing or even both axial and radial viewing. This development has not been something widely taken up by the geochemical industry. While the detection limits are lower, matrix effects and matrix mismatches with internal standards were greatly increased. (Dubuisson et al. 1997, 1998). Any benefit of lower detection limits was lost for geochemical samples in the overall decrease in accuracy.

Quadrupole ICP-MS – Rare Earth Geochemistry

Commercial quadrupole ICP-MS instruments were first introduced the mid-eighties. The nineties saw the introduction of the second generation of these instruments allowing for more rugged and routine operation. As well, computing power improved to ease the reporting of combined instrumental results, from ICP-MS when the levels for critical pathfinders elements are low, or from ICP-OES for elements at the top end of the ICP-MS dynamic range. What is of note in the area of multi-element determinations and quadrupole ICP-MS is its capabilities for rare earth element (REE) analysis and the implications of more sensitive data for geochemistry.

There are two distinct procedures for the REE determinations. One is ICP-MS analysis following a fusion for the determination of total rare earth content, the other is INAA. In the late 90's, detection limits and precision between INAA and ICP-MS fusion methods were comparable. (Dai Kin et al, 1998) Prior to the advent of ICP-MS, INAA was the method of choice for REE work even though not all REEs could be measured. La, Ce, Nd, Sm, Eu, Tb, Yb and Lu were analyzed by INAA. If the elements, Pr, Gd, Dy, Ho, Er and Tm were required they had to be done by ICP-MS. The data obtained showed that for elements determined by both methods, the accuracy was similar for the light REE and better for the middle and heavy REE by INAA. This is partly due to the heavy REE occurring at low concentrations. Since then, detection limits for the REE by ICP-MS following a fusion have dropped by at least an order of magnitude, mitigating this issue. That factor, in addition to the better element coverage offered by ICP-MS, has made it the method of choice. Standard lithochemical studies will now combine XRF data for the majors and selected traces with the REE and other traces from the fusion ICP-MS

procedures. Complete characterization over and over again uses the ICP-MS procedures. (Jones et al. 2006, Spangenberg and Herlec, 2006, Torres-Ruiz, 2006).

The relative low cost of generating rare earth information has allowed geoscientists to start using them as pathfinders where they might previously not been considered. An example of this is a study by Nkoane et al. (2007) that includes the analysis of soils and plants using the ICP-OES and ICP-MS combination packages. The authors were able to analyze for 62 elements to determine which ones were most representative of mineralization. One key finding is that the REE elements were found in concentrations above normal for all plants. It is the easy access to this wide range of elements that is allowing correlations and identifications of patterns in the REE elements that previously were not available.

Sample Introduction

Other innovations in instrumentation this past decade include improvements in sample introduction. One such device is an autosampler from Elemental Scientific Inc., (Omaha, NB) that dramatically improves uptake and washout times leading to at least a factor of two increase in instrument productivity. A vacuum pump is used to draw the sample which increases the speed that liquid can be moved to the instrument. A loop system is used to eliminate air in the uptake line and reduce the length of tubing requiring washout. As well, by clever sequencing, the samples are pulled into the loop while the sample ahead is being analysed, greatly reducing instrument cycle times.

Multi-element and Multi-variant Quality Control

Significant advancements have been made in the evaluation of multi-element geochemical data. Procedures such as factor analysis, multi-variant parameters, Kriegering have become routine. Conversely, procedures for reviewing the QC data from multi-element generally remain relatively simple.

Most client quality control is done with a Shewhart control chart for each individual element being determined. This has real limitations when dealing with multi-element data. When control chart parameters for failure are set at 95% confidence levels you can expect to have one failure in 20 due to statistical variation. The problems with multi-element data is that this 1/20 failure rate adds up for each element. The net result is a failure rate of $(0.95)^n$ where n is the number of elements. For a group of 50 elements (not uncommon now) there should be a one failure every 0.077 or 93% of the time. (Fletcher, 1981). The elements are correlated so the situation is not that bad but this does point out the problems posed by simple control charts for each element. As well, using this approach there is the problem of review and management of multiple control charts.

Hotelling's T- statistic is an expansion of the Student's T distribution to multivariate space. The problem with its application is the requirement to calculate the matrix of the cross interaction between each element. This is difficult for application to on-line control. However, the first term is the sum of the variations from the mean for each term in the equation.

Review of these differences, keeping the sign of the deviation from the mean can be useful for detecting controls that are showing trends high or low but are not enough to completely generate a failure.

COLLISION CELLS AND REACTION CELLS FOR QUADRUPOLE ICP-MS

Polyatomic and isobaric interferences were a major barrier in ICP-MS analysis limiting the sensitivity for many elements, particularly light elements. These problems were resolved by the development of reaction cells and collision cells that sit between the plasma and the quadrupole mass spectrometer. The purpose of these cells is to react, in some way, with the polyatomic or isobaric species from the ion beam before they enter the final analyzer, resulting in improved detection limits for traditionally difficult elements, including As, Cr, Fe and Se (Tanner et al. 2000). There does need to be work done to define the chemistry required for the elimination of the different interferences and the gas required may differ for each element. The spectral interference on 75As from 40Ar35Cl is eliminated by using helium in the reaction cell. The argon dimer 40Ar40Ar that affects 80Se is reduced by methane. Rather than trying to develop and run separate chemistries for the different interferences, use of a high resolution mass spectrometer would seem to be a better solution.

There are a number of spectroscopic interferences, those caused by isobaric nuclides that can not be resolved even with the resolution of double focusing mass spectrometers. (Moens and Jakubowski, 1998.) These interferences can only be avoided by using isotopes not suffering from these interferences or by chemically separating the analyte from the interfering element prior to the determination. Rb/Sr age determination is an example of this. The method requires the Rb/Sr concentration ratio and accurate and precise determination of the 87Sr/86Sr isotope ratio in samples containing 87Rb at similar concentration levels. Time consuming chemical separation of Sr and Rb is required for thermal ionisation mass spectrometry (TIMS), the method of choice. However, Moens, L.J. et al. (2001) describe a method using the ion-molecule reaction in the dynamic reaction cell for an elegant solution to this problem. Sr⁺ ions are converted with CH₃F to SrF⁻ ions that can be measured free of the isobaric interference from Rb⁺ ions that do not react with CH₃F. No chemical separation is required and the resulting rock age is identical within experimental uncertainty, to the TIMS age, and the precision is only slightly poorer. The method could be a useful alternative when the ultimate precision is not required or for the screening of large numbers of samples in exploration programs.

In another paper, Bandura et al. (2000), show the dynamic reaction cell can be used to improve the precision of isotope ratio measurements to within the theoretical limit defined by counting statistics error. The most significant factor affecting the precision of isotope and inter-element ratio measurements of scanning ICP-MS is the fluctuation of the ion density in the beam extracted from the ICP. In this example, the reaction cell collisions rather than chemistry are used to smooth out ion beam fluctuations and improve isotope ratio precision.

All four Pb isotopes were measured in the same acquisition with precision results for the ratios only slightly above counting statistics errors. In the case of Fe determinations, ArO⁺ and ArN⁺ interferences were removed by reaction with NH₃ gas in the reaction cell. This coupled with the collisional dampening from the cell, allowed for precise isotope ratio measurement of the normally interfered isotopes of ⁵⁴Fe, ⁵⁶Fe and ⁵⁷Fe, with internal precision limited only by counting statistics.

ICP-MS INSTRUMENTATION – TRENDS TO HIGHER RESOLUTION

ICP-MS instruments are now available with three distinct types of mass spectrometers. The most common is the quadrupole. This mass spectrometer is capable of unit mass resolution and uses a scanning electron multiplier as a detector. The next up in price and complexity is a magnetic sector mass spectrometer equipped with a similar scanning type detector - HR-ICP-MS (high-resolution). The magnetic sector spectrometer is capable of superior mass resolution, down to fractions of mass units and has much higher ion throughput resulting in lower detection limits. It can be used in high resolution mode to resolve interferences (Moen, 1998) or at lower resolution to provide lower detection limits. The third type of ICP-MS system is a multi-collector magnetic sector ICP-MS (MC-ICP-MS). Here the resolving power of the magnetic sector spectrometer is coupled with individual detectors (Faraday cups) as in TIMS for each mass of interest, to provide the ultimate in precision and accuracy.

Isotope Measurements with ICP-MS

Quadrupole mass analyzers are designed and optimized for the scanning of large mass ranges. As a consequence, they are less stable than magnetic sector mass analyzers and less well suited to highly precise and accurate isotope ratio measurement. Given the price differences between the two types of instrumentation and the availability, numerous researchers have worked on optimizing isotope measurements with a quadrupole ICP-MS. Begley and Sharp (1997) studied the forms of instrumental instability and bias which limit the accuracy and precision of isotope ratio measurements made by quadrupole based ICP-MS. In their study, the results for the Pb isotopes are the most precise to date done by quadrupole ICP-MS but measurements made using a multiple collector magnetic sector ICP-MS instruments continue to be of superior accuracy and precision.

Lead isotope studies represent an interesting application for geologist and geochemists. It was first used as a geochronological tool over eighty years ago; better understanding of the issues related to non-radiogenic Pb has limited its application to minerals that formed with very little Pb. However, more practically, the Pb isotope composition of rocks can be used to trace the sources of metals in ores, ore genesis and to help discriminate barren from mineralized systems. Thermal ionization mass spectrometry (TIMS) is the technique of choice but its application is limited by the necessary and extensive chemical pretreatments required prior to the analysis.

These time consuming and labor intensive procedures cause it to be impractical for routine use in exploration programs. Townsend et al. (1998) describe a fast and reliable method for the precise measurement of Pb isotope ratios in geological samples by HR-ICP-MS. Their work shows that Pb isotopes can be measured relatively quickly by HR-ICP-MS and to a precision approaching TIMS for a substantially smaller cost. This in turn opens up the possibility of the routine use of Pb isotopes in geochemical exploration surveys for new mineral deposits.

Encinar et al. (2001) directly compared the three types of ICP-MS instruments; quadrupole, double focusing and multicollector spectrometers and evaluated the total combined uncertainty for lead isotope ratio measurements. A method is described for the determination of the combined uncertainty associated with the measurement of lead isotope ratios after correction for dead time effects and mass bias using Tl as an internal standard. It was found that for the multicollector instrument, uncertainty in the natural Tl ratio was the only source of error. Measurement of the isotope ratio was the main source of uncertainty for the quadrupole and double focusing single collector instruments.

HR-ICP – ROUTINE AND COMMERCIALY AVAILABLE

It is often stated that routine application and use of magnetic sector instruments in commercial laboratories and academic institutions will not occur because of the high cost of these instruments and the problems in operating them, specifically maintaining stability and the high throughputs required in commercial applications. The capital cost of these instruments for the large commercial groups and research teams is no longer a real impediment to their purchase and application. Of more concern and problematic for routine work would be the lack of stability, drift and generally low throughput associated with them. Schramel and Wendler (1998) studied the causes of short and long term drift in a HR-ICP-MS. They concluded that instability and drift are independent of the mass spectrometer, but strongly dependent on the sample introduction system, the ICP-torch and the cones. This bodes well for commercial applications. The success of high volume commercial laboratories depends on the control and management of these very factors on a daily basis for routine ICP-OES and quadrupole ICP-MS measurements. Given this expertise, it is not out of the question that productivity will be comparable to that of quadrupole ICP-MS instruments in the future.

Halogens

A solution for the determination of halogens may finally be at hand. Determination of halogens by quadrupole ICP-MS has been limited due the severe molecular interferences created by the plasma gas, water and acids used. The nominal mass to charge ratio of these interfering polyatomic ions are mostly less than 80 atomic mass units, which can be identical to the halogen elements. The resolving power of the new generation of sector-

field ICP mass spectrometers can provide a resolution capable of interference free, accurate determinations for these elements. Magnetic sector instruments also offer high sensitivity and low background levels resulting in low detection limits. Halogens have high ionization potentials compared to most elements. An example is sodium at 5.14 eV and fluorine at 17.42 eV. A procedure for HR-ICP-MS determination of sub ppm to percentage levels of F, Cl, Br and I in organic compounds has been described (Bu et al., 2003). Fluorine is determined in medium resolution mode and Cl, Br and I in high resolution mode. It should be possible to apply this technology to geological materials, perhaps following a fusion.

Multicollector-ICP-MS – applications

The potential for isotope analysis by ICP-MS has long been clear ever since it was first introduced. However, development of a useful tool required resolution of a number of limitations related to using the plasma as the ion source. Polyatomic and molecular ions are formed in the plasma that interfere with the ions of interest. With double focusing magnetic sector fields, mass spectrometer resolution can be increased to resolve molecular isobaric interferences. Flickers in signal intensity are significant in ICP-MS and limit the precision of the isotope ratio measurements when jumping between peaks. In multicollector ICP-MS, ions are detected simultaneously by individual, faraday detectors at each mass of interest and this eliminates plasma noise. Recent instrumental developments have made MC-ICP-MS competitive to TIMS as a reference technique for isotope measurements.

Walczyk (2004) compares TIMS and MC-ICP-MS as techniques. MC-ICP-MS allows ratio measurements at precision below 50 ppm, which previously was only possible using TIMS. TIMS requires the isotopes of interest to be separated from the matrix, whereas with MC-ICP-MS the sample can be presented directly to the instrument. In recent years more than 80 MC-ICP-MS have been sold. However, before we declare the demise of TIMS about 60 of them were sold in that time period (Walczyk, 2004). Isotopic fractionation in TIMS is of the order of parts per thousands and stable, whereas in MC-ICP-MS, fractionation can easily be in the percent range and variable, requiring corrective techniques. Walczyk (2004) makes the point that quality standards and definitions for MC-ICP-MS must be defined before the potential of the method is fully recognized. There are applications where each has merit. The high ionization potential of hafnium makes MC-ICP-MS more suitable for this element. In contrast osmium isotope ratio measurements are easier by TIMS.

One place where MC-ICP-MS has application is in the analysis of small samples and when it is connected to a laser, for example the high resolution laser ablation procedure for dating of monazite crystals described by Paquette and Tiepolo, 2007. When TIMS is applied, even for single monazite grains, it records multiple overgrowths. In contrast, when MC-ICP-MS is coupled to a laser ablation microprobe it is capable of producing stable and reliable isotope measurements.

CONCLUSIONS

It is clear that instrumental developments over the last decade now allow the rapid, low cost determination of virtually the entire periodic table apart from gases. This capability provides the exploration geochemist with unprecedented choice in using various combinations of elements in exploration. It would be no exaggeration to claim that interpretation of this wealth of data has yet to catch up with the advances in instrumental techniques.

The most important development has been the realization of the potential of ICP-MS technology to determine large elemental packages with excellent precision and accuracy.

More recent developments with this technology, and specifically in MC-ICP-MS, are opening the door to a new dimension in exploration geochemistry, notably the use of isotopic systems as sensitive tracers of geochemical processes.

REFERENCES

- Baker, T., Mustard, R., Brown, V., Pearson, N., Stanley, C.R., Radford, N.W. and Butler, I., 2006, Textural and chemical zonation of pyrite at Pajingo: a potential vector to epithermal gold veins. *Geochemistry: Exploration, Environment, Analysis*, 6, 283-293.
- Bandura, D.R., Baranov, V.I. and Tanner, S.D., 2000, Effect of collisional damping and reactions in a dynamic reaction cell on the precision of isotope ratio measurements, *J. Anal. At. Spectrom.*, 15, 921-928.
- Barnard, T.W., Crockett, M.I., Ivaldi, J.C. and Lundberg, P.L., 1993 a, Design and evaluation of an echelle grating optical system for ICP-OES. *Anal. Chem.* 65: 1225-1230.
- Barnard, T.W., Crockett, M.I., Ivaldi, J.C., Lundberg, P.L., Yates, D.A., Levine, P.A. and Sauer, D.J., 1993 b. Solid-state detector for ICP-OES, *Anal. Chem.* 65: 1231-1239.
- Begley, I.S. and Sharp, B.L., 1997, Characterisation and correction of instrumental bias in inductively coupled plasma quadrupole mass spectrometry for accurate measurement of lead isotope ratios, *J. Anal. At. Spectrom.*, 12: 395-402.
- Brown, P.G., Hildebrand, A.R., Zolensky, M.E., Grady, M., Clayton, R.N., Mayeda, T.K., Tagliaferri, E., Spalding, R., MacRae, N.D., Hoffmann, E.L., Mittlefehldt, D.W., Wacker, J.F., Bird, J.A., Campbell, M.D., Carpenter, R., Gingerich, H., Glatiotis, M., Greiner, E., Mazur, M.J., McCausland, P.J.A., Plotkin, H., and Mazur, T.R., 2006, The Fall, Recovery, Orbit, and Composition of the Tagish Lake Meteorite: A New Type of Carbonaceous Chondrite. *Science*, 290: 320-325.
- Bu, X., Wang, T. and Hall, G., 2003. Determination of halogens in organic compounds by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). *J. Anal. At. Spectrom.* 18: 1443-1451.
- Cornelius, M., Porto, C.G., Dunn, C.E., Butt, C.R.M., Oates, C., and Coelho, R., 2007, Soil and biogeochemical signatures of the Aripuanã base metal deposit Mato Grosso, Brazil. *Geochemistry: Exploration, Environment, Analysis*, 7: 179-192.
- Dai Kin, F., Prudêncio, M.I., Gouveia, M.A. and Magnusson, E., 1998, Determination of rare earth elements in geological reference materials: a comparative study by INAA and ICP-MS. *Geostandards Newsletter* 23: 47-58.

- Dubuisson, C., Poussel, E. and Mermet, J., 1997, Comparison of axially and radially viewed inductively coupled plasma atomic emission spectrometry in terms of signal-to-background ratio and matrix effects. *J. Anal. At. Spectrom.* 12: 281-286.
- Dubuisson, C., Poussel, E. and Mermet, J., 1998, Comparison of ionic line-based internal standardization with axially and radially viewed inductively coupled plasma atomic emission spectrometry to compensate for sodium effects on accuracy. *J. Anal. At. Spectrom.* 13: 1265-1269.
- Encinar, J.R., Alonso, J.I.G., Sanz-Medel, A., Main, S. and Turner, P.J., 2001, A comparison between quadrupole, double focusing and multicollector ICP-MS instruments. Part I. Evaluation of total combined uncertainty for lead isotope ratio measurements. *J. Anal. At. Spectrom.* 16: 315-321.
- Fletcher, W.K., 1981. Analytical methods in geochemical prospecting in ed. G.J.S. Govett, *Handbook of exploration Geochemistry* Elsevier, New York.
- Jones, S., Gemmell, J.B. and Davidson, G.J., 2006, Petrographic, geochemical, and fluid inclusion evidence for the origin of siliceous cap rocks above volcanic-hosted massive sulphide deposits at Myra Falls, Vancouver Island, British Columbia, Canada. *Economic Geology* 101: 555-584.
- Moens, L., and Jakubowski, N., 1998, Double-focusing mass spectrometers in ICP-MS. *Anal. Chem.* 70: 251A-256A.
- Moens, L.J., Vanhaecke, F.F., Bandura, D.R., Baranov, V.I. and Tanner, S.D., 2001, Elimination of isobaric interferences in ICP-MS, using ion-molecule reaction chemistry: Rb/Sr age determination of magmatic rocks, a case study. *J. Anal. At. Spectrom.*, 16, 991-994.
- Nkoane, B.B.M., Wibetoe, G., Lund, W., and Torto, N., 2007, A multi-element study on metallophytes from mineralized areas in Botswana using ICP-AES and ICP-MS. *Geochemistry: Exploration, Environment, Analysis*, 7: 49-56.
- Paquette, J.L. and Tiepolo, M., 2007. High resolution (5 μm) U-Th-Pb isotope dating of monazite with excimer laser ablation (ELA)-ICPMS. *Chem. Geol.* 3-4: 222-237.
- Prendergast, Kylie, 2007, Application of litho-geochemistry to gold exploration in the St Ives goldfield, Western Australia. *Geochemistry: Exploration, Environment, Analysis*, 7: 99-108.
- Roberts, S., Palmer, M.R., and Waller, L., 2006, Sm-Nd and REE Characteristics of Tourmaline and Scheelite from the Björkdal Gold Deposit, Northern Sweden: Evidence of an Intrusion-Related Gold Deposit? *Economic Geology*, 101: 1415-1425.
- Schramel, P. and Wendler, I., 1998. Some investigations on stability and precision of an HR-ICP-MS. *Fresenius J. Anal. Chem.* 360: 152-155.
- Spangenberg, J.E. and Herlec, U. 2006. Hydrocarbon biomarkers in the Topla-Mežica zinc-lead deposits, northern Karavanke/Drau Range, Slovenia: Paleoenvironment at the site of ore formation. *Economic Geology* 101: 997-1021.
- Tanner, S.D., Baranov, V.I. and Vollkopf, U., A dynamic reaction cell for inductively coupled plasma mass spectrometry (ICP-DR-MS) Part III. Optimization and analytical performance, 15, 1261-1269.
- Torres-Ruiz, J., 2006, Geochemical constraints on the genesis of the Marquesado iron ore deposits, Betic Cordillera, Spain: REE, C, O, and Sr Isotope Data. *Economic Geology* 101: 667-677.
- Townsend, A.T., Yu, Z., McGoldrick, P. and Hutton, J.A., 1998. Precise lead isotope ratios in Australian galena samples by high resolution inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.* 13, 809-813.
- Walczyk, T., 2004, TIMS versus multicollector-ICP-MS: coexistence or struggle for survival? *Anal Bioanal Chem*, 378: 229-231.