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Journal of Analytical Atomic Spectrometry

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IN THIS ISSUE

ISSN 0267-9477 CODEN JASPE2 25(3) 217–436 (2010)



Cover

See Abdelrahman *et al.*, pp. 260–268.
A mass cytometer resolves signals from a mixture of ^{153}Eu -containing microspheres as an internal standard and biological cells labeled with an ^{193}Ir -containing metallointercalator. Authors acknowledge the contribution of Ihab El-Minyawi and Isaac Herrera in designing this cover.
Image reproduced by permission of A. I. Abdelrahman from *J. Anal. At. Spectrom.*, 2010, **25**, 260.



Inside cover

See Thickett *et al.*, pp. 269–281. Metal-labeled polymer particles carrying labeled proteins and antibodies are analyzed by a novel detection method based on ICP-MS. These particles have use in assays for the detection of biological moieties.
Image reproduced by permission of S. C. Thickett from *J. Anal. At. Spectrom.*, 2010, **25**, 269.

EDITORIALS

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Young Analytical Scientists issue

Spiros Pergantis introduces the 3rd YAS Special issue.



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Contributors to the young analytical scientists special issue



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CRITICAL REVIEW

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Recent advances in isotope dilution analysis for elemental speciation

Pablo Rodríguez-González* and J. Ignacio García Alonso

This review presents and critically discusses new concepts, methodologies and trends that have appeared during the last five years of scientific development in the field of isotope dilution analysis for elemental speciation.



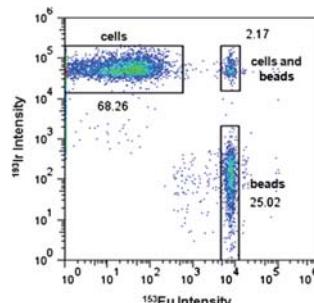
PAPERS

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Metal-containing polystyrene beads as standards for mass cytometry

Ahmed I. Abdelrahman, Olga Ornatsky, Dmitry Bandura, Vladimir Baranov,* Robert Kinach, Sheng Dai, Stuart C. Thickett, Scott Tanner and Mitchell A. Winnik*

A bivariate plot of mass cytometry results for cells mixed with polymer beads.

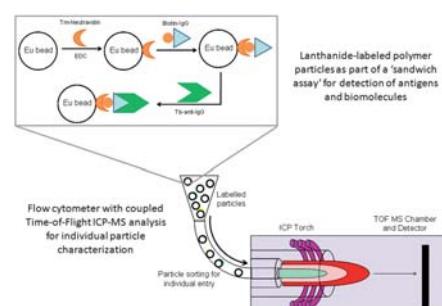


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Bio-functional, lanthanide-labeled polymer particles by seeded emulsion polymerization and their characterization by novel ICP-MS detection

Stuart C. Thickett* Ahmed I. Abdelrahman, Olga Ornatsky, Dmitry Bandura, Vladimir Baranov* and Mitchell A. Winnik*

A novel method for the analysis of metal-labeled polymer particles by ICP-MS is presented. These particles have relevant surface chemistry for bioconjugation and subsequent use in assays for the detection of biological moieties.

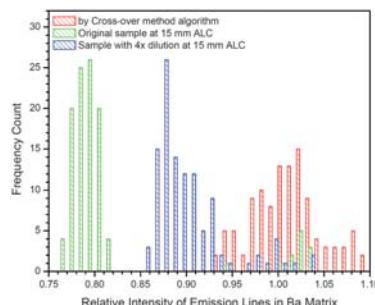


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Algorithm to determine matrix-effect crossover points for overcoming interferences in inductively coupled plasma-atomic emission spectrometry

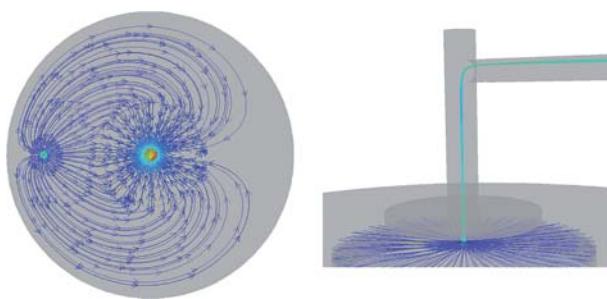
George C.-Y. Chan* and Gary M. Hieftje

An algorithm for automated identification of matrix-effect-free crossover points in ICP-AES is developed. Improvements in analytical accuracy are readily observed.



PAPERS

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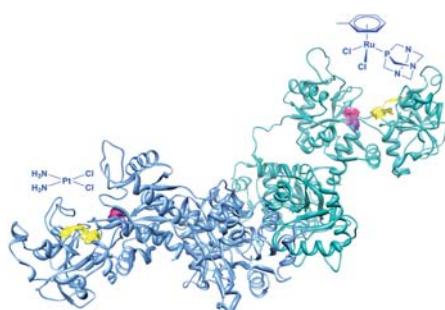


Numerical simulation analysis of flow patterns and particle transport in the HEAD laser ablation cell with respect to inductively coupled plasma spectrometry

Helmut Lindner,* David Autrique, Jorge Pisonero, Detlef Günther and Annemie Bogaerts

A laser ablation cell is analyzed by CFD simulations, characterizing particle transport through its modules. Additionally, a modified setup with extremely short washout-time is proposed from the findings.

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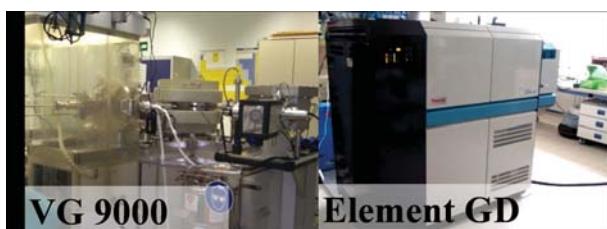


Reactivity of anticancer metallodrugs with serum proteins: new insights from size exclusion chromatography-ICP-MS and ESI-MS

Michael Groessl, Mattia Terenghi,* Angela Casini,* Lisa Elviri, Ryszard Lobinski and Paul J. Dyson

The metal binding of anticancer metallodrugs, cisplatin and RAPTA-T, to serum proteins albumin and transferrin was investigated by ICP-MS and ESI-MS.

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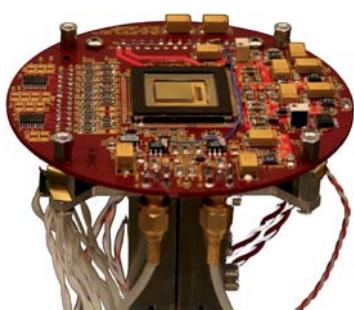


Comparison of different calibration strategies for the analysis of zinc and other pure metals by using the GD-MS instruments VG 9000 and Element GD

Tamara Gusarova,* Thomas Hofmann, Heinrich Kipphardt, Cornel Venzago, Ralf Matschat and Ulrich Panne

The calibration of GD-MS instruments VG 9000 and Element GD with self prepared synthetic standards were shown to be very advantageous in comparison to other quantification approaches.

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Optimization of Ag isotope-ratio precision with a 128-Channel array detector coupled to a Mattauch-Herzog mass spectrograph

Gregory D. Schilling,* Steven J. Ray, Roger P. Sperline, M. Bonner Denton, Charles J. Barinaga, David W. Koppenaal and Gary M. Hieftje

Peak integration methods and drift are examined for the use of a 128-channel Faraday-strip array detector for precise isotope ratio measurements.

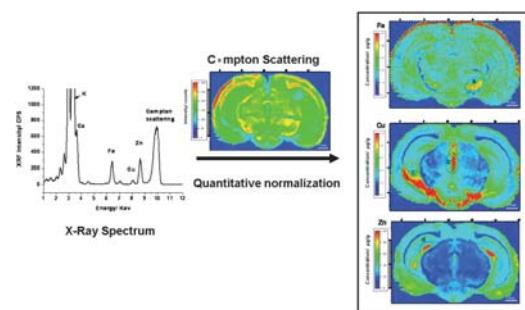
PAPERS

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Quantitative imaging of element spatial distribution in the brain section of a mouse model of Alzheimer's disease using synchrotron radiation X-ray fluorescence analysis

Hua-Jian Wang, Meng Wang,* Bing Wang, Xiang-Yu Meng, Yun Wang, Ming Li, Wei-Yue Feng,* Yu-Liang Zhao and Zhi-Fang Chai

The element distributions in a mouse brain are quantitatively determined with SRXRF using Compton scattering normalization.

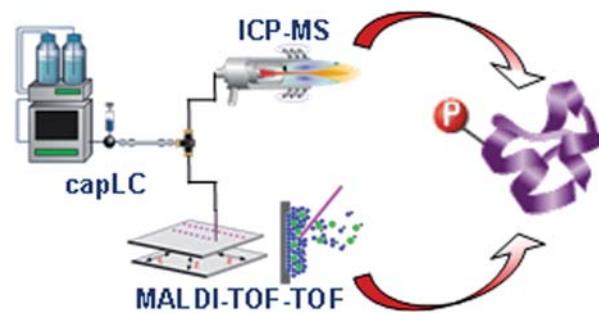


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Hyphenation of capillary-LC with ICP-MS and parallel on-line micro fraction collection for MALDI-TOF-TOF analysis—complementary tools for protein phosphorylation analysis

Daniel Pröfrock*

A new and simple approach for the complementary application of ICP-MS and MALDI-TOF *via* flow splitting and micro fraction collection and its application for protein phosphorylation analysis is presented in this work.

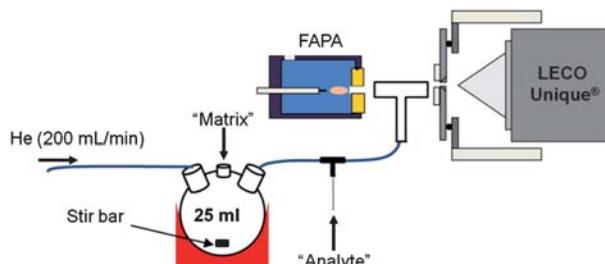


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Ionization matrix effects in plasma-based ambient mass spectrometry sources

Jacob T. Shelley* and Gary M. Hieftje

Ionization matrix effects were investigated for three, plasma-based ambient mass spectrometry ionization sources: FAPA, DART, and LTP. Surprisingly, all three sources exhibited significant ion suppression for equimolar amounts of matrix and analyte.

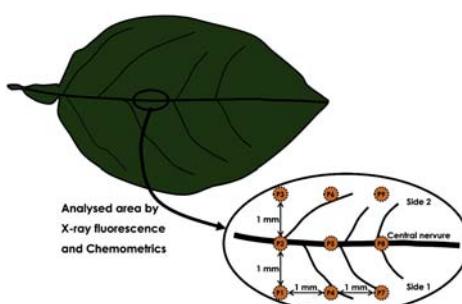


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Investigation of the stages of citrus greening disease using micro synchrotron radiation X-ray fluorescence in association with chemometric tools

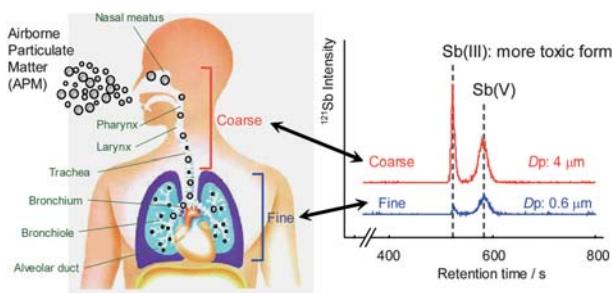
Fabiola Manhas Verbi Pereira*
and Débora Marcondes Bastos Pereira Milori

The information obtained using μ SR-XRF spectra profiles and the chemometric tools allowed the construction of predictive models to identify infected trees by citrus greening disease with and without symptoms.



PAPERS

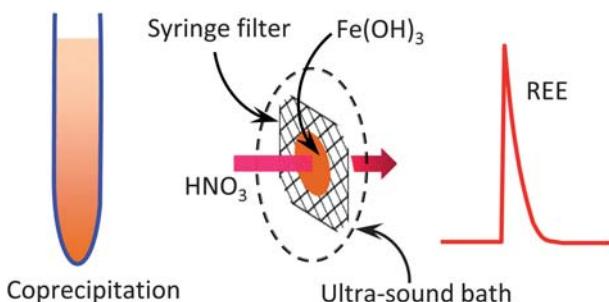
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Concentration distributions of dissolved Sb(III) and Sb(V) species in size-classified inhalable airborne particulate matter

Akihiro Iijima,* Keiichi Sato, Tomohiro Ikeda, Hikaru Sato, Kunihisa Kozawa and Naoki Furuta

Concentration distributions of Sb(III) and Sb(V) in size-classified airborne particulate matter were elucidated by using a multistage aerosol sampler and HPLC-ICP-MS.

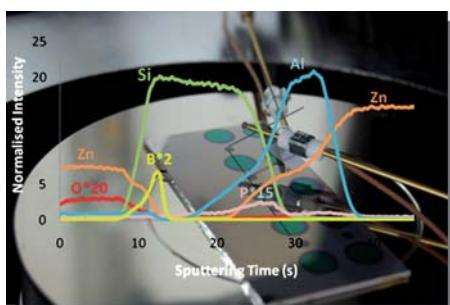
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On-line elution of iron hydroxide coprecipitate carrier for determination of REEs in natural water by mix-gas ICP-MS

Yanbei Zhu,* Kazumi Inagaki, Hiroki Haraguchi and Koichi Chiba

Iron hydroxide coprecipitate carrier enriching REEs was collected in a syringe filter, which was subsequently connected into an ultra-sound assisted on-line elution system with mix-gas ICP-MS for measurement of REEs.

370


Pulsed radiofrequency glow discharge optical emission spectrometry for the direct characterisation of photovoltaic thin film silicon solar cells

Pascal Sánchez, Beatriz Fernández,* Armando Menéndez, Rosario Pereiro and Alfredo Sanz-Medel

Pulsed radiofrequency glow discharge-optical emission spectrometry is successfully investigated for the in-depth profile characterisation of thin film solar cells based on hydrogenated amorphous silicon.

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Isotopic characterisation of in-house purified progesterone for $^{13}\text{C}/^{12}\text{C}$ isotope ratios by multicollector ICP-MS

Rebeca Santamaría-Fernandez* and Thierry Le Goff

For the first time, MC-ICP-MS has been used to provide absolute carbon ratios in an organic compound to be used as an isotopic reference for metrological studies.

PAPERS

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 **Certification of natural isotopic abundance inorganic mercury reference material NIMS-1 for absolute isotopic composition and atomic weight**

Juris Meija,* Lu Yang, Ralph E. Sturgeon and Zoltán Mester

A candidate reference material of natural isotopic composition for inorganic mercury has been characterized using multi-collector ICP-MS based on a state-of-the-art regression model for calibration.

MICHAEL MAIER

EST IN MERCURIO QUICQUID QUÆRUNT SAPIENTES
(1618)

what wisemen seek in Mercury is found

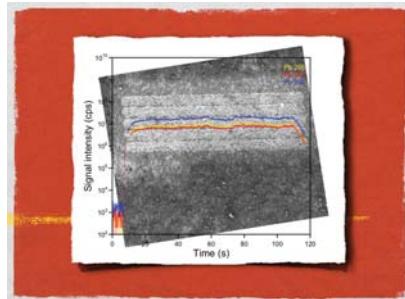
Atalanta Fugiens

390

Isotope ratio determination by laser ablation-single collector-inductively coupled plasma-mass spectrometry. General capabilities and possibilities for improvement

Maite Aramendía,* Martín Resano and Frank Vanhaecke

Some methodological approaches for improving isotope ratio results with Laser Ablation-Single Collector-ICP-MS are presented in this work.



TECHNICAL NOTES

405

 **Shorter signals for improved signal to noise ratio, the influence of Poisson distribution**

Martin Tanner*

Shorter signals do not necessarily provide improved signal to noise ratio. It exists an optimum signal duration which depends on the level of the signal background.



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NH₄F assisted high pressure digestion of geological samples for multi-element analysis by ICP-MS

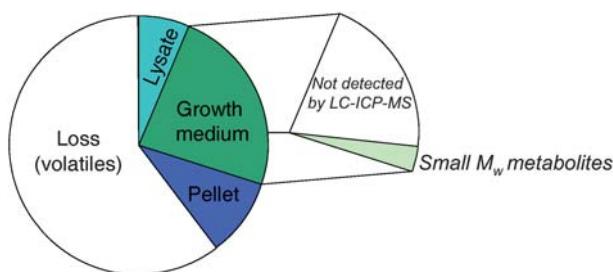
Zhaochu Hu,* Shan Gao, Yongsheng Liu, Shenghong Hu, Laishi Zhao, Yanxiang Li and Qi Wang

Decomposition methods using mixtures of less toxic and safer NH₄F and HNO₃ in high pressure digestion bombs were established for different types of rock reference materials.



TECHNICAL NOTES

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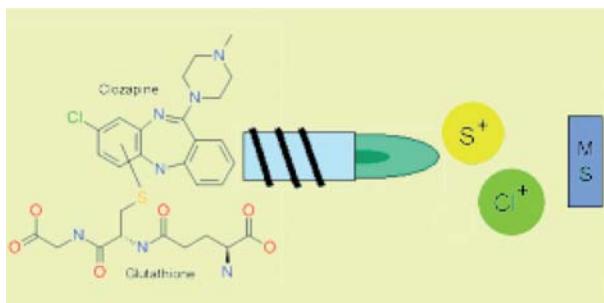


Selenium metabolism in hepatocytes incubated with selenite, selenate, selenomethionine, *Se*-methylselenocysteine and methylseleninic acid and analysed by LC-ICP-MS

Charlotte Gabel-Jensen* and Bente Gammelgaard

The amount of small molecular weight selenium metabolites produced in an in vitro metabolism model was estimated. Small M_w metabolites constituted only a small part of the dosed selenium.

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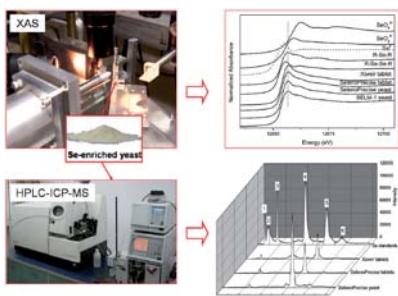


A comparison between HPLC-dynamic reaction cell-ICP-MS and HPLC-sector field-ICP-MS for the detection of glutathione-trapped reactive drug metabolites using clozapine as a model compound

Kenny De Wolf, Lieve Balcaen,* Elke Van De Walle, Filip Cuyckens and Frank Vanhaecke

A novel method for the detection of reactive drug metabolites, based on the combination of HPLC and ICP-MS for the monitoring of Cl and S has been proposed and successfully applied to a clozapine metabolite mixture containing several glutathione conjugates.

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Direct quantitative speciation of selenium in selenium-enriched yeast and yeast-based products by X-ray absorption spectroscopy confirmed by HPLC-ICP-MS

Li Yu-Feng,* Wang Xiaoyan, Wang Liming, Li Bai, Gao Yuxi and Chen Chunying*

Direct quantitative Se speciation by XAS through PCA and least-squares linear combination fitting the Se-enriched yeast samples were achieved, which is in agreement with HPLC-ICP-MS analysis.

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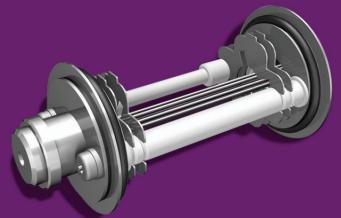
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Qualifier ions in ICP-MS

Effective interference removal in helium mode allows the measurement of secondary isotopes to validate ICP-MS data



Qualifier ions in ICP-MS

The Agilent 7700x ICP-MS incorporates a 3rd generation Collision/Reaction Cell (CRC) which operates effectively in helium (He) mode. In contrast to reactive cell gases, which work only for specific reactive interferences, He mode is universal, as it effectively filters out all polyatomic ions regardless of their reactivity. The benefits of He mode for multi-element analysis of complex, variable and unknown sample matrices have been well documented, but He mode has a further important benefit. He mode simultaneously removes all polyatomic interferences from all isotopes of each analyte, thereby making secondary ions (isotopes) available for many analytes.

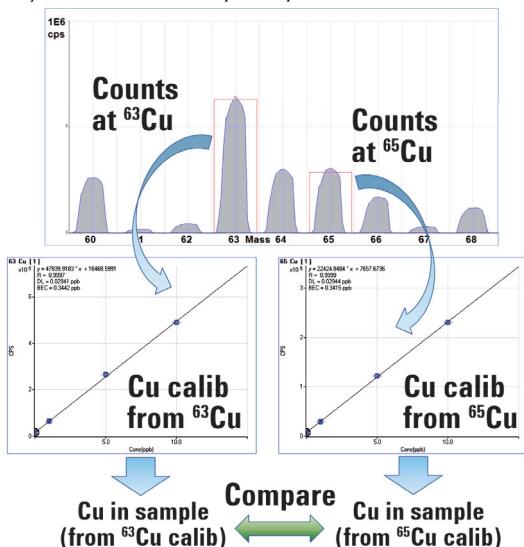


Figure 1. Use of qualifier ions in ICP-MS

The use of qualifier ions to confirm the identity of a target analyte is common practice in organic mass spectrometry, where the mass of the target ion does not provide unequivocal analyte identification. The simple spectra of ICP-MS means that primary or preferred isotopes give much more certain identification of the target analyte, but the quantification of many elements can be affected by the presence of matrix-based polyatomic interferences. By quantifying an element independently using both the primary and secondary isotopes, the results can be compared; good agreement validates the data, indicating that the reported concentration was not affected by any interference.

Comparison of Results for Isotope Pairs

In the data presented here, ten complex synthetic sample matrices were analyzed, using He, reaction and no gas modes. The relative % difference (RPD) between the results from the primary and qualifier isotopes of several analytes were compared for each matrix; good agreement indicates effective removal of interferences

from both isotopes. Figure 2 shows excellent agreement between the $^{65}\text{Cu}/^{63}\text{Cu}$ results in He mode (green bars) in all matrices (all He mode results were <2% RPD). This is in contrast to both no gas mode (blue bars) and reaction mode (H_2 cell gas, red bars), where the incomplete removal of interferences from one or other isotope led to large differences between the results (RPD between ^{65}Cu and ^{63}Cu results were up to 182% RPD in no gas mode and up to 915% RPD in reaction mode). Negative RPD values (e.g. $^{65}\text{Cu}/^{63}\text{Cu}$ in H_3PO_4 measured in H_2 and no gas mode) indicate an interference on the primary isotope.

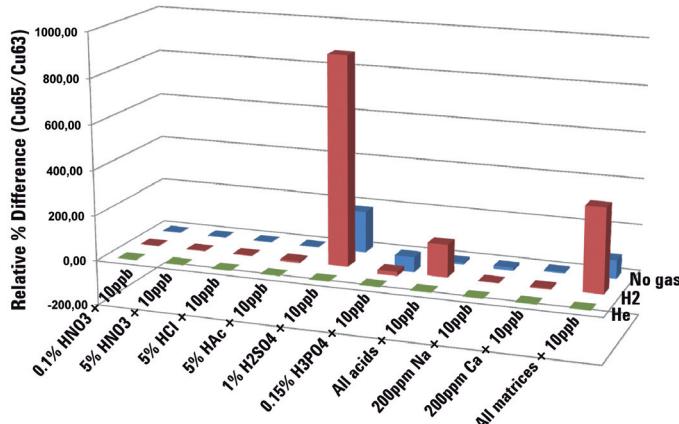


Figure 2. Comparison of $^{65}\text{Cu}/^{63}\text{Cu}$ results in 3 modes and 10 matrices

Figure 3 shows the same comparison for $^{53}\text{Cr}/^{52}\text{Cr}$, again demonstrating the excellent agreement between the results from the 2 isotopes measured in He mode (<3% difference in all matrices). As with Cu, the residual (or newly-created) interferences in no gas and reaction mode gave poor agreement between the Cr isotopes (up to 453% RPD in H_2 mode and 744% RPD in no gas mode).

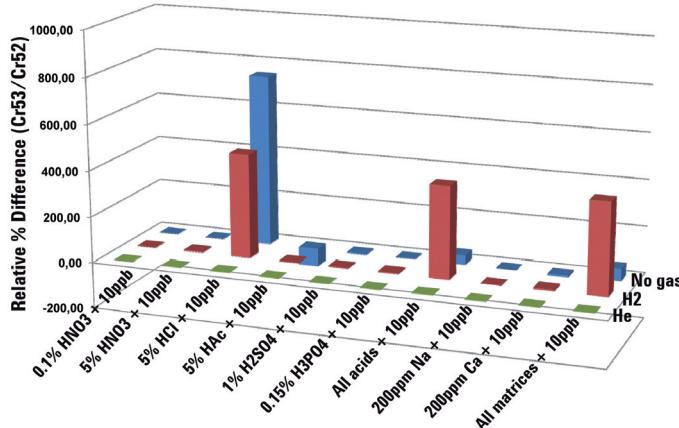
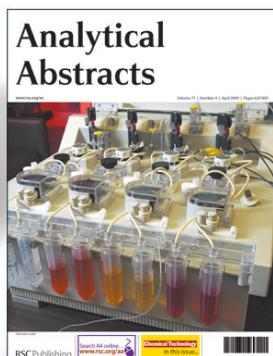


Figure 3. Comparison of $^{53}\text{Cr}/^{52}\text{Cr}$ results in 3 modes and 10 matrices

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