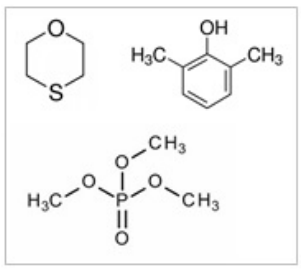
BrJAC

Brazilian Journal of Analytical Chemistry
an International Scientific Journal

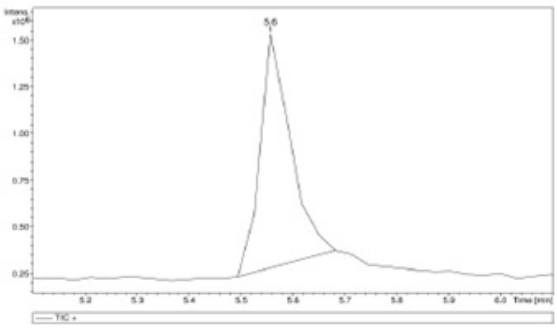
World free of chemical weapons



Chemical Weapon Residues in the Environment

Mobile GC-MS System

Qualitative On-site Analysis



Use of Mobile Gas Chromatograph Coupled to Mass Spectrometer to Detect Toxic Compounds in Environmental Samples

Carla da Silva Pinheiro, Carlos Geraldo Campos de Mello, Victor Hugo Pella Legramandi, Natalia Fintelman Rodrigues, Ana Paula Santiago De Falco

April – June 2020 Volume 7 Number 27

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Brazilian Journal of Analytical Chemistry

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Scope

BrJAC is dedicated to the diffusion of significant and original knowledge in all branches of Analytical Chemistry. BrJAC is addressed to professionals involved in science, technology and innovation projects in Analytical Chemistry at universities, research centers and in industry.

BrJAC publishes original, unpublished scientific articles, reviews and technical notes that are peer reviewed in the double-blind way. In addition, it publishes interviews, points of view, letters, sponsor reports, and features related to analytical chemistry. Once published online a DOI number is assigned to the paper.

Manuscripts submitted for publication in BrJAC cannot have been previously published or be currently submitted for publication in another journal. For manuscript preparation and submission, please see the Guidelines for the Authors section at the end of this edition.

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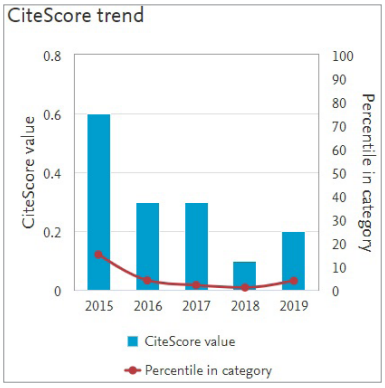

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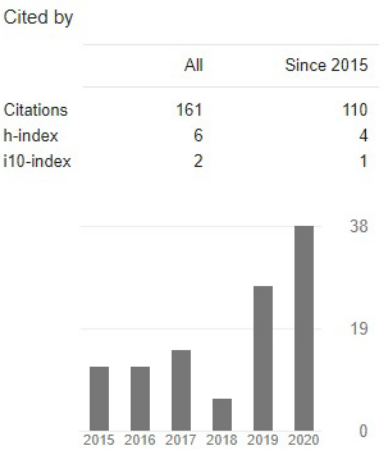

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CONTENTS

Editorial
Large-Scale Assays 1-2
Elias Ayres Guidetti Zagatto

Interview
Professor Jose Manuel Riveros, whose important research achievements in chemistry are internationally recognized, recently gave an interview to BrJAC 3-9
Jose Manuel Riveros Nigra

Point of View
Decompartmentalized Knowledge and Core Analytical Chemistry Concepts 10-11
George L. Donati

In Memoriam
BrJAC pays Tribute to Full Professor Ronei J. Poppi (1961 – 2020) 12-13
Fabio Augusto

Articles
Stability of Vitamin C in Enriched Jelly 14-19
Lucile Tiemi Abe-Matsumoto, Yara Alves de Araújo, Magda Leite Medeiros

Use of Mobile Gas Chromatograph Coupled to Mass Spectrometer to Detect Toxic Compounds in Environmental Samples 20-30
Carla da Silva Pinheiro, Carlos Geraldo Campos de Mello, Victor Hugo Pella Legramandi, Natalia Fintelman Rodrigues, Ana Paula Santiago De Falco

Optimization of Extraction Induced by Emulsion Breaking Variables for Subsequent Determination of Crude Oil Salinity by Ion Chromatography 31-39
Anna Carolina de Oliveira Pinheiro Ramos, Gabriel Rocha Figueira Caldeira, Carolina Ramos de Oliveira Nunes, Wagner da Silva Terra, Murilo de Oliveira Souza

Feature
2020 Pittcon Conference and Exposition was a success in Chicago 40-42

Sponsor Reports
Unknown Profiling of Drinking Water Using High Resolution LC-MS/MS and New Software 43-50
Thermo Scientific

Quantitative Comparison of Hormones in Drinking Water Between MS/MS and Orbitrap Technology 51-56
Thermo Scientific

Rare Earth Element Determination in Heavy Crude Oil by USN-ICP-MS After Digestion Using Single Reaction Chamber Technology 57-59
Milestone

CONTENTS (Continuation)

Releases
Planet Orbitrap – A science-based website focusing on Orbitrap Mass Spectrometers 60
Thermo Scientific

Leading Performance – Orbitrap Exploris 240 Mass Spectrometer 62
Thermo Scientific

Milestone ultraWAVE is the Benchmark in Microwave Digestion 64
Milestone

Pittcon Conference & Expo 2021 – Don't Miss the World's Leading Event on Laboratory Science..... 66

SelectScience® Pioneers Online Communication and Promotes Scientific Success since 1998..... 68

CHROMacademy Helps Increase your Knowledge, Efficiency and Productivity in the Lab..... 70

Notices of Books 72

Periodicals & Websites 73

Events..... 74

Guidelines for the Authors 75-77

Brazilian Journal of Analytical Chemistry
2020, Volume 7, Issue 27, pp 1-2
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BrJAC

EDITORIAL

Large-Scale Assays

Elias Ayres Guidetti Zagatto
Full Professor
Centre for Nuclear Energy in Agriculture, University of Sao Paulo
Piracicaba, SP, Brazil

A decade ago (June 18th - the Chemist Day in Brazil), BrJAC was launched as "the seed of our dream of fostering integration between academia, research centers, and industry at this time of growth for graduate programs at the international level" [1].

As the first Brazilian scientific journal entirely dedicated to Analytical Chemistry, it underwent a remarkable development, as demonstrated by the continuous increase in *e.g.* impact factor, widespread dissemination, and recognition by the scientific community. This reflects the quality of the scientific articles, reviews and technical notes, as well as opinions of the community through editorials, points of view, letters, interviews, sponsor reports and releases. The BrJAC involvement in scientific meetings, the "Young Talent in Analytical Chemistry Award", the enthusiastic collaboration of the analytical community, and the logistic of manuscript handling, as well as the dedication of the editing staff should also be highlighted.

Regarding enhancement of the scientific interaction between universities, research institutes and companies, an important aspect refers to the management of laboratories dedicated to large-scale analysis, as testified by me at the Centre for Nuclear Energy in Agriculture (CENA), University of Sao Paulo during the seventies. As a member of CENA's analytical team, I experienced an important moment in the context of Analytical Chemistry: the development of a novel concept of automated chemical analysis - flow injection analysis - and its pioneer exploitation for large-scale assays [2,3].

The innovation led to an outstanding increase in the productivity of the laboratory, allowing analysis relevant to all CENA projects to be performed in a very short time, with a low cost-benefit ratio, and excellent figures of analytical merit. Other Institutions and private initiatives started to request analysis, thus establishing a healthy situation combining research development and services.

Analysis of atypical samples with unexpected matrix composition, concentrations of potential interfering species and/or out-of-range analyte concentrations required other specific strategies. This was the driving force towards additional developments in flow analysis, providing themes for more realistic and relevant research. This aspect culminated with the proposal of expert flow analyzers, which enable the real-time implementation of flow and manifold modifications. Consequently, the research quality, idea dissemination, and integration of people with different formations have been improved.

Nowadays, it is recommended that, regardless of the involved analytical instruments, an academic or an industrial laboratory for large-scale analysis should contemplate two goals: performing repetitive assays of typical samples, and carrying out research to solve difficulties that are inherent to atypical samples. All individuals involved should be able to work in both situations. This results in a natural establishment of research teams, an increased university-enterprise relationship, a more realistic and relevant research, and improvements in the laboratory capacity, among others. Last, but not least, the quality of the analytical results, the originality, relevance and suitability of the research, and the importance of the related scientific papers will certainly be better.

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The role of BrJAC in the near future is therefore to continue supporting analytical chemistry, both on the academic and industrial side. The quality of each published issue should always be higher than that of the previous one. Enjoy reading this issue.

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3. Cerqueira, A. *Braz. J. Anal. Chem.*, **2010**, *1* (1) pp XIV-XVII.

Elias Ayres Guidetti Zagatto has a degree in Agronomic Engineering from the University of São Paulo (1971), a master degree in Nuclear Energy in Agriculture from the University of São Paulo (1974) and a doctoral degree in Analytical Chemistry from the University of Campinas (1981). He is currently a Professor at the Center for Nuclear Energy in Agriculture, University of São Paulo, and a Member of the Brazilian Academy of Sciences. His research activities mainly include the design and development of flow analyzers, with applications on relevant samples in the agronomic, environmental, pharmaceutical and industrial areas.

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BrJAC

INTERVIEW

Professor Jose Manuel Riveros, whose important research achievements in chemistry are internationally recognized, recently gave an interview to BrJAC

Jose Manuel Riveros Nigra
Institute of Chemistry, University of São Paulo, SP, Brazil

Jose Manuel Riveros Nigra, better known as Professor Riveros, is an Emeritus Professor at the Institute of Chemistry of the University of São Paulo (IQ-USP), Brazil, where he was the Director from 1982 to 1986, and Head of the Fundamental Chemistry Department twice, from 1981 to 1982 and from 1992 to 1993. Prof. Riveros has been an advisor to the Brazilian Association of Synchrotron Light Technology – ABTLuS, and a former member of the Editorial Boards of *Spectrochimica Acta A*, *Journal of Mass Spectrometry*, *Mass Spectrometry Reviews*, *International Journal of Mass Spectrometry* and *Journal of the Brazilian Chemical Society*, and President Emeritus of the Brazilian Society of Mass Spectrometry.

Born and raised in Asunción, Paraguay, Prof. Riveros obtained his Bachelor's degree in Chemistry from the University of California at Berkeley in 1962, and his Ph.D. degree in Chemistry from Harvard University in 1966, under the supervision of Professor E. Bright Wilson Jr., a world renowned physical and quantum chemist of the 20th century. Prof. Riveros is internationally known for his important contributions to the field of gas phase ion-molecule reactions using a combination of mass spectrometric techniques and electronic structure calculations.

Prof. Riveros continues to contribute to the IQ-USP as a Senior Professor and his research has been primarily dedicated to the study of chemical reactions in the gas phase. His studies have primarily involved the chemistry of gas-phase ions, mechanisms of gas-phase ionic reactions, semiclassical molecular dynamics of simple reactions, gas-phase ion solvation, the thermodynamic characterization of solvated ions in solution and pKa calculations, molecular spectroscopy using various techniques and applications of multiphoton infrared excitation using lasers and blackbody radiation in the study of gas-phase ions.

With more than one hundred publications, his contributions in the field of physical chemistry have earned him, in addition to a reaction known in the literature as the "Riveros reaction", several awards and honors including election to full membership in the Brazilian Academy of Sciences in 1980 and the National Order of Merit, Category "Grão Cruz", in 2005. In addition, his work has been recognized by a Special Issue in his honor of the *International Journal of Mass Spectrometry* (Volume 418, July 2017) and a Special Issue of the online journal ARKIVOC (Volume 2020(ii)).

Cite: Nigra, J. M. R. Professor Jose Manuel Riveros, whose important research achievements in chemistry are internationally recognized, recently gave an interview to BrJAC. *Braz. J. Anal. Chem.,* 2020, *7* (27) pp 3-9. doi: http://dx.doi.org/10.30744/brjac.2179-3425.interview.jmrnigra

Would you tell us a little about your childhood and early school years?

I did my primary and secondary studies at the “Colégio San José” in Asunción, Paraguay, a school of French origin that emphasized a strong classical education, various sporting activities, and what the French define as “esprit de corps”.

What early influences encouraged you to study science? Did you have any influencers, such as a teacher?

I consider my physics and chemistry teachers of the last two years of high school to be the main motivators of my interest in these areas. I was particularly attracted to issues related to atomic structure, the development of nuclear physics and the discovery of new chemical elements (transuranium elements).

When did you decide to study chemistry? What motivated you? How was the beginning of your career?

By the end of my high school years I was interested in pursuing studies in Physics or Chemistry. However, there were no specific courses in Paraguay at that time (1957-1958) directed toward further education in Physics or Chemistry as pure sciences. In the end, I opted to enter the Faculty of Chemistry and Pharmacy of the University of Asunción in 1958. While the Faculty of Chemistry and Pharmacy offered courses leading to degrees in Industrial Chemistry or Biochemistry and Pharmacy, I was very much aware that these major areas were not exactly what I had in mind.

What has changed in your profile, ambitions, and performance since the beginning of your career?

The big change came in early 1959. I had applied for a scholarship offered annually by the United States Embassy in Paraguay. These scholarships had little or almost no demand because they were only for one North American academic year (September to June). I was fortunate to be awarded a scholarship specifically for the University that I had indicated as my first choice: the University of California at Berkeley. For me, it was very exciting to know that I was going to the institution where Ernest Lawrence developed the cyclotron, and where Glen Seaborg triggered the discovery of transuranium elements. I was highly successful academically during the term of the scholarship, so it was extended until I completed my undergraduate studies at Berkeley. Furthermore, I was honored as the top student of the 1962 Chemistry class. Reflecting on my studies at Berkeley, I can particularly highlight an undergraduate research project carried out in the laboratory of Prof. Bruce Mahan, the Quantum Chemistry classes of Prof. Dudley Herschbach (Nobel Prize 1986), and the Physical Organic Chemistry course given by Prof. Donald Noyce.

In 1962, I was admitted as a graduate student at Harvard University with a full scholarship. There, I undertook my Ph.D. thesis on molecular structure studies by microwave spectroscopy under the supervision of Prof. Bright Wilson. My experience at Harvard, from 1962 to 1966, was very stimulating because of the opportunity to interact with some of the great names in Chemistry and Physics. I also had the great pleasure of sharing an apartment in Cambridge, MA, USA, with two other graduate students and great friends, one of whom, Tom Steitz, would earn the Nobel Prize in Chemistry in 2009. I must also mention the support and encouragement that I always received from my father, Dr. Manuel Riveros, who is considered the master of surgery in Paraguay.

Jose M. R. Nigra and Thomas A. Steitz at Harvard University in 1963.

Could you briefly comment on recent developments in analytical chemistry, considering your contributions?

I will mention four areas that are of current importance and to which I believe we have made some fundamental contributions. Obviously, many other areas at the forefront of chemical research such as the chemistry of biomolecules, the chemistry and properties of nanoparticles, the enormous growth of computational chemistry, the revival of electrochemistry, advances in catalysis, among others.

- The elucidation of reaction mechanisms from an intrinsic point of view has had a huge impact on our understanding of reactions of interest on the interface of chemistry and biology. In this respect, our paper published in 1978 (Takashima, K.; Riveros, J.M. "Gas Phase Pathways for Ester Hydrolysis", *J. Am. Chem. Soc.* **1978**, *100*, 6128), and other later papers related to this (Pliego, J.R.Jr.; Riveros, J.M. "The Gas Phase Reaction between Hydroxide Ion and Methyl Formate: A Theoretical Analysis of the Energy Surface and Product Distribution", *Chem. Eur. J.* **2001**, *7*, 169), represent a breakthrough in the interpretation of the mechanisms of simple biochemical model systems.

- The experimental article published in 1973 (Riveros, J.M.; Breda, A.C.; Blair, L.K. "Formation and Relative Stability of Chloride Cluster Ions in the Gas Phase by Ion Cyclotron Resonance", *J. Am. Chem. Soc.* **1973**, *95*, 4066) represents a historic milestone in the theoretical development of the potential energy surfaces of ionic reactions in the absence of a solvent. This is a subject that has had enormous development since the 1980s. Progressively higher-level computational methods have been widely used in recent years, and have even allowed for the simulation of reaction dynamics that do not strictly obey traditional statistical theories (for example, de Souza, M.A.F.; Correra, T.C.; Riveros, J.M.; Longo, R.L. "Selectivity and Mechanisms Driven by Reaction Dynamics: The Case of the Gas-Phase OH^- + CH_3ONO_2 Reaction", *J. Am. Chem. Soc.* **2012**, *134*, 19004).

- Vibrational ion spectroscopy based on dissociation induced by infrared multiphoton absorption, is now widespread. Some of the potential applications have stemmed from our early papers [for example, (a) Gaumann, T.; Riveros, J.M.; Zhu, Z. "The Infrared Multiphoton Dissociation Spectra of Bromopropene Isomeric Cations", *Helv. Chim. Acta* **1990**, *73*, 1215; (b) Gaumann, T.; Zhu, Z.; Kida, M.C.; Riveros, J.M. "Kinetic and Spectroscopic Characterization of the Allyl Bromide Molecular Ion", *J. Am. Soc. Mass Spectrom.* **1991**, *2*, 372. (c) Morgon, N.H.; Linnert, H.V.; Giroldo, T.; Riveros, J.M. "The Isomerization of the Molecular Ion of Allyl Bromide", *J. Phys. Chem.* **1996**, *100*, 18048].

- Theoretical modeling of reactions in solution, and particularly those involving ions in aqueous solution, has represented a huge challenge and a subject of increasing interest. The development of a robust methodology to calculate the Gibbs energy of ion solvation (Pliego, J.R.Jr.; Riveros, J.M. "The cluster-continuum model for the calculation of the solvation free energy of ionic species", *J. Phys. Chem. A* **2001**, *105*, 7241) has been hugely successful and has been extensively used to calculate aqueous phase pK_a's and the energy profile of reactions in solution (for example, Pliego, J.R.Jr.; Riveros, J.M. "A Theoretical Analysis of the Free Energy Profile for the Different Pathways in the Alkaline Hydrolysis of Methyl Formate In Aqueous Solution", *Chem. Eur. J.* **2002**, *8*, 1945).

What are your lines of research? You have published many scientific papers. Would you highlight any?

My research activities at the Institute of Chemistry at the University of São Paulo have gradually decreased since 2010, after I reached compulsory retirement. However, I have maintained my interest in the characterization of chemical reactions at the fundamental level, of which some examples have been illustrated above. As I no longer have a laboratory under my responsibility, I have carried out both experimental and theoretical work in collaboration with other researchers from Brazil and abroad. In addition

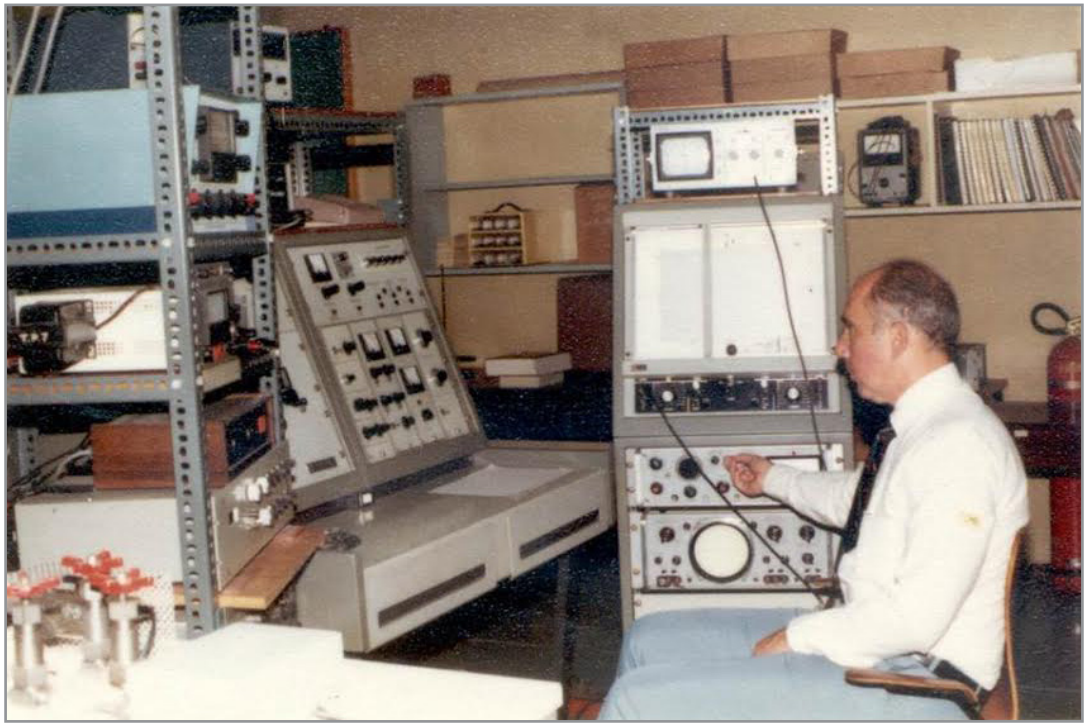
to the articles previously cited, I would like to cite four papers that have been particularly rewarding for me and that have been internationally recognized:

- Riveros, J.M. “Anharmonic of the Out-of-Plane Vibration of the Methyl Radical”, *J. Chem. Phys.* **1969**, *51*, 1269. This is my first paper published as a faculty member at the University of São Paulo and was helpful in elucidating the planar structure of the methyl radical.

- Faigle, J.F.G.; Isolani, P.C.; Riveros, J.M. “The Gas Phase Reaction of F^- and OH^- with Alkyl Formates”, *J. Am. Chem. Soc.* **1976**, *98*, 2049. This is the fundamental article that describes what would become known as the ‘Riveros reaction’. Much credit should be given to Prof. Paulo Celso Isolani who did a lot of the groundwork on these reactions during his Ph.D. thesis under my supervision.

- Riveros, J.M.; Ingemann, S.; Nibbering, N.M.M. “Formation of Gas Phase Solvated Br^- and I^- in Ion/Molecule Reactions of Halobenzenes. Revised Heat of Formation of Benzyne”, *J. Am. Chem. Soc.* **1991**, *113*, 1053. The work described in this publication was originally started in our laboratory in 1976 and resulted in the demonstration that benzyne has a much higher thermochemical stability than originally proposed. This paper opened new paths in the study of benzyne-related reactions.

- Giroldo, T.; Xavier, L.A.; Riveros, J.M. “An Unusually Fast Nucleophilic Aromatic Displacement Reaction: The Gas-Phase Reaction of Fluoride Ions with Nitrobenzene”, *Angew. Chem. Int. Ed.* **2004**, *43*, 3588. A pioneering work that demonstrated the possibility of a concerted mechanism in nucleophilic aromatic reactions and that has led to the discovery of a series of similar reactions in condensed phases.



Prof. Riveros at work on the ICR instrument at the IQ-USP laboratory, 1984.

Do you keep yourself informed about the progress of research in chemistry? What is your opinion about the current progress of chemistry research in Brazil? What are the recent advances and challenges in scientific research in Brazil?

I continue to follow the main Chemistry journals, both those that are of a general scope and those that are more specialized in physical chemistry. I also continue to be asked to be a referee of manuscripts submitted to first rate journals such as the *J. Am. Chem. Soc*, *Chem. Eur. J*., *J. Phys. Chem. A and B* and others.

It is clear that issues related to biomolecules occupy the greatest emphasis today, but there are important advances in the area of materials, in the area of organic synthesis and the functionalization of molecules, and in the introduction of new analytical methodologies. I understand that there has been a great advance of research in Chemistry in Brazil, especially in the last 20 years, covering all areas of Chemistry. This can be easily illustrated by the large number of publications by Brazilian researchers in a variety of journals dedicated to all areas of Chemistry. It is particularly noteworthy that this advance is observed across the country, from North to South, despite the differences in research conditions and the support available in the different Brazilian regions.

"I understand that there has been a great advance of research in Chemistry in Brazil, especially in the last 20 years, covering all areas of Chemistry."

I believe that the great challenge, in addition to the continuous support necessary for the progress of research, is to achieve greater international insertion. This is increasingly important because Brazil is geographically far from the major centers of scientific strength. Brazilian researchers often find it difficult to attend international meetings, with the exception perhaps of those in the State of São Paulo, where financial support from the São Paulo Research Foundation (FAPESP) has been significant. On the other hand, and despite the need to give due credit to the work carried out in the country, I am sometimes concerned by the occasional exaggerated local "radio broadcasting" of results claiming miraculous applications that are based on circumstantial evidence.

For you, what have been the most important recent achievements in analytical chemistry research? What are the landmarks?

Research in Analytical Chemistry has had a spectacular development in the last 30 years, to the point where *Analytical Chemistry* – an American Chemical Society journal – has a large following by the whole chemical community. This journal, along with other main journals covering analytical chemistry, have reached high relevance and notoriety among international journals.

From the present major areas of analytical chemistry, I can highlight the evolution of mass spectrometry as an analytical tool applicable to a wide range of problems. The advances in instrumentation and in ionization methods in mass spectrometry presently allow for qualitative and quantitative analyses with great selectivity, sensitivity and reliability, with applications ranging from simple substances to highly complex biomolecules.

There are in Brazil, and in the world, several conferences on chemistry. To you, how important are these meetings to the scientific community? How do you see the development of national chemistry meetings in Brazil?

Scientific meetings, in Brazil and around the world, are extremely important for several reasons, such as: updating of the researcher; opportunity to openly expose results; opportunity to establish contacts with other researchers; and the possibility of stimulating new ideas and new areas of research based on works presented at these meetings. There are currently excellent meetings in Brazil, especially those dedicated to specific areas of Chemistry. It has been possible to attract renowned scientists from different countries as Invited Lecturers and the topics discussed have covered the frontiers of the different areas. Large meetings, such as the annual meeting of the Brazilian Chemical Society or the six-monthly meetings of the American Chemical Society have become huge, and I believe that the mini-symposia embedded in these meetings turn out to be the most important events.

Would you mention the recognitions have you received for your professional achievements?

- Full Member of the Brazilian Academy of Sciences since 1980.
- Founding Member of the São Paulo State Academy of Sciences in 1976.
- Rheinboldt-Hauptmann Prize, 1998.
- Simão Mathias Medal of the Brazilian Chemical Society, 2001.
- National Order of Scientific and Technological Merit, Category "Grão Cruz", 2005.
- Emeritus Professor at the Institute of Chemistry, University of São Paulo, 2015.
- Special issue of the International Journal of Mass Spectrometry in my honor, Volume 418, July 2017.
- Special issue of the journal ARKIVOC (Archive for Organic Chemistry) in my honor, Volume 2020.

For you, what is the importance of the national funding agencies for the scientific development of Brazil?

Funding agencies are essential for the progress of science in the country, and Chemistry in Brazil would not have had the development we see today without this support. In particular, I would like to mention robust programs such as: the Support Program for Scientific and Technological Development (PADCT), the Thematic Grants and the Research, Innovation and Dissemination Centers (CEPIDs) supported by the São Paulo Research Foundation (FAPESP); the National Council for Scientific and Technological Development (CNPq) Millennium Institutes; the Coordination for the Improvement of Higher Education Personnel (CAPES) and the CNPq scholarship programs. On the other hand, I believe that "Ciência sem Fronteiras" (Science Without Frontiers) program did not have the expected impact considering the enormous amount of resources allocated to the program. It is also noticeable that the participation of the private sector in promoting research in Brazil is still very timid despite of the importance of Chemistry to Brazil. Only Petrobras, the Brazilian energy company, has financed projects of various types, and more recently the Serrapilheira Institute, the first private non-profit institution, has been geared towards fostering science in Brazil.

"There are currently excellent conditions in Brazil to achieve a solid specialization in Chemistry, given the existence of excellent research centers in several universities in the country."

At the moment, the situation for scientific research in Brazil is one of decreasing investment. How do you see this situation, and what would you say to young researchers?

Everything points to an exceedingly difficult situation in the short term, due to cuts in the budget for science and technology by the federal government. This situation becomes even more dramatic considering the effect that the new coronavirus pandemic will have on Brazil's economy. The sharp depreciation of the Brazilian currency will also be an unfavorable factor for the purchase of imported supplies and equipment, and which may not be fully accounted by the current research grants. At this moment, I fear that young researchers will have great difficulty in obtaining significant research funds and it may be necessary for them to pool efforts in joint projects with other researchers from Brazil and abroad.

What advice would you give to a young scientist who wants to pursue a career in analytical chemistry?

There are currently excellent conditions in Brazil to achieve a solid specialization in Chemistry, given the existence of excellent research centers in several universities in the country. The most important thing at the outset is interest, scientific curiosity and a real motivation for Chemistry. I would recommend that undergraduate students start early participating in a good quality research group to become familiar with current problems, techniques and methodologies in Chemistry, and to see how research projects are actually carried out. Chemistry, like other human activities, requires a lot of dedication. Science has no timetable - when you find a good idea or a good experiment, try to do it completely. It should always be remembered that Chemistry as a successful science is 5% inspiration and 95% effort.

There is also an untapped potential to develop advances in chemistry in the private sector, and for those

with an entrepreneurial spirit, I believe there will be enormous possibilities in Brazil in the future. But above all, a young scientist must have ambition and passion for what she/he does.

How would you like to be remembered?

I hope I have contributed to the education of many generations of chemists in Brazil and have been able to motivate them and encourage a critical spirit, curiosity and enthusiasm for the unknown, both for those who joined the job market after graduation and for those who chose an academic career.

How important is it for you to have been a professor and researcher at an institution like the University of São Paulo?

I joined the University of São Paulo (USP) initially as a Visiting Professor at the former Faculty of Philosophy, Sciences and Letters, in November 1967, after completing a one-year postdoctoral tenure at Columbia University, New York. I became an Assistant Professor in 1968 and in 1970 I joined the newly created Institute of Chemistry at the same university (IQ-USP). I was promoted to Full Professor in 1977.

My experience as a professor and researcher at USP was very rewarding for several reasons: i) I had the satisfaction of participating in the beginning of formal Ph.D. programs at USP starting in 1970; ii) the high quality of USP students; iii) the research tradition established by the pioneers of IQ-USP, among them Professors Paschoal Senise, Ernesto Giesbrecht, Simão Mathias and Giuseppe Cilento; iv) the Ph.D. students, postdocs and undergraduate research interns who have been part of my research group since its creation in 1970 and to whom I am very grateful; v) the incomparable technical assistance received first by Antônio Geraldo Ayrosa, and from 1990 onwards by Jair Menegon, without whom it would not have been possible to develop research and instrumentation in our group.

Prof. Riveros in front of the FT ICR instrument at the IQ-USP laboratory, 2007.

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POINT OF VIEW

Decompartmentalized Knowledge and Core Analytical Chemistry Concepts

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One of the most important skills a researcher can wish for is the ability to take knowledge from one field and seemly apply it to another. In fact, this is true for researchers and for everyone else. If you keep an open mind, experiences from different periods of your life may be successfully used to solve a difficult problem, even if these (your experiences and the problem at hand) seem totally unrelated at first. I will use an event from my own life as an example (even though it is not a scientific one). Different from other adults driving for the first time on ice/snow, I had no trouble doing it. All because of my teenage years' experience driving my father's VW Beetle (Fusca) in slippery mud. In this spirit, think about how much of the knowledge used to create everything, from planes to computers, comes from different fields. This type of decompartmentalized, unprejudiced approach has always been a powerful force driving scientific and human progress.

As another example of a decompartmentalized approach for solving problems, several recent studies in the biomedical field describe the use of machine learning tools helping researchers better understand gene expression and disease progression, as well as facilitating the development of alternative diagnosis and treatment methods [1,2]. On the other hand, as an atomic spectrometry researcher, I feel elemental information is missing in such studies and could significantly contribute to a more complete overview of medical conditions [3]. As analytical chemists, we could also intensify our collaborations with other fields and offer a unique, specialized perspective on their issues, and at the same time expand the capabilities of our own methods. I know collaborations take time and effort to flourish, particularly because each field has its own interests and its own timeline. However, collaborations are long-term investments for all parties involved. It takes patience, but it is worth it.

In the biomedical field, for example, there are many opportunities for collaboration. Atomic spectrometry researchers are well positioned in this case, as only a relatively small number of studies involving trace element analysis and medical conditions have been reported. In such collaborations, one has the chance to learn and apply new tools, such as supervised and unsupervised machine learning. In combination with the simultaneous multi-element instrumentation available to spectroscopists, these tools allow for developing powerful methods. In addition, with new tools in hand (and keeping an open mind), we can revisit some old problems. Machine learning may help, for example, identify and minimize matrix effects [4], or facilitate the selection of internal standards [5]. There are numerous machine learning techniques that could significantly expand the application of our methods. From unsupervised approaches, such as *t*-distributed stochastic neighbor embedding (*t*-SNE) and uniform manifold approximation and projection (UMAP), to efficient supervised techniques, such as neural networks, support vector machines and random forests. The list is long, and is growing everyday with increased interest for applications in every field. However, as in other areas of life, one has to use a new tool with caution so it produces the desired results. These techniques are as good as the data one feeds them. Therefore, solid analytical chemistry concepts should guide their use, not the other way around.

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To finalize my "*point of view*" on using knowledge from different fields to solve the most varied problems, I would like to say we should strive to apply some of the core concepts of analytical chemistry during these difficult times we are living today. Just as a single point is incapable of indicating a trend, a single person cannot have all the answers. Let us listen to many voices (as we would collect several data points) before reaching a conclusion. Furthermore, let us not give much weight to extreme positions. Just as outliers (when given much importance significantly skew the data), extreme voices often contribute to inaccurate conclusions.

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IN MEMORIAM

BrJAC pays Tribute to Full Professor Ronei J. Poppi (1961 – 2020)

Ronei Jesus Poppi ***CV*** was born in a peripheral neighborhood in the city of Campinas (SP, Brazil), in a lower middle-class family – his father was the neighborhood barber; he spent his childhood and adolescence with several of his future colleagues at the University of Campinas (Unicamp). In 1978, he started a technical course in Industrial Chemistry at the then Technical Industrial College "Conselheiro Antonio Prado" (Coticap, today ETECAP). Soon after completing technical education, he joined the Bachelor of Chemistry course at Unicamp having graduated in 1986 as one of the best in his class. He immediately started his Master's degree, co-supervised by professors Fernando Faigle (already deceased) and Roy Bruns – who, in particular, would become a landmark scientific and personal reference for the then Master's student. For his Doctorate, he joined the group of Prof. Célio Pasquini – at the time a group that was still being formed but which was already on the way to becoming one of the great centers of reference in analytical instrumentation in Brazil. In his Doctoral thesis (defended in July 1993), Ronei built a Hadamard Transform Spectrometer – a suggestion by the then postgraduate student and future colleague at the Institute of Chemistry at Unicamp (IQ-Unicamp) Pedro A.M. Vazquez (who collaborated in several stages of the system design). This work involved many stages from the construction of optical devices and high-level microcomputer programming to the development of multivariate data processing tools (a topic that had already been studied by Ronei in his Master's thesis). Ronei's enormous capacity and talent did not go unnoticed by the academy, and after a short period at the Federal University of Pernambuco (Recife, Brazil), he returned to Campinas and was admitted as a Professor in the Department of Analytical Chemistry at IQ-Unicamp, in 1994.

In the mid-1980s, the advent of relatively inexpensive microcomputers with much higher processing capacity than previously existing alternatives added to the demand from industry and academia for approaches that could provide very fast and reliable answers to problems in chemical and biochemical analysis. The experience and deep knowledge acquired by Ronei in his Master's and Doctorate were decisive in showing him that his future as a researcher was in Chemometrics, a newly emerged area of research, which, at that time, was still viewed with some suspicion and prejudice by analytical chemists of traditional education. Therefore, even though he already had a solid base in Chemometrics, Ronei spent 1996 as a postdoctoral fellow with Professor Desiré Luc Massart's group at the Free University of Brussels, Belgium – at the time, one of the greatest chemometrists in the world. After this internship, on his return to Unicamp, he actually started his activities as an independent researcher and soon established himself as a reference in Chemometrics in Brazil and the world. Ronei supervised more than sixty Master's and Doctoral dissertations and theses and published 280 scientific articles – almost all of them dealing with cutting-edge developments and the application of several chemometric tools to relevant analytical problems in the chemical and pharmaceutical industry and in environmental and biochemical analyses. In many of them, relatively unexplored instrumental techniques were used: he was one of the pioneers in Brazil of Near Infrared Absorption Spectrometry (NIR), and more recently, in analytical Raman Spectroscopy and its variants. A more detailed examination of his scientific production shows that many of his works were the result of collaborations with colleagues at Unicamp and outside.

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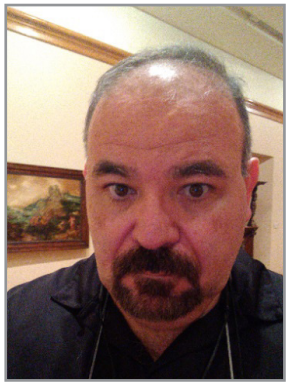
His enormous and inventive influence on research in Analytical Chemistry and Chemometrics in Brazil can be recognized by the fate of Master's and Doctoral students graduating from his research group: many of them are now important Professors and researchers at universities and public and private research centers throughout Brazil. Ronei was often requested as a lecturer and organizer of scientific meetings and events; rare was the week when he did not receive an invitation to act as a reviewer of manuscripts submitted to specialized journals and on thesis and examining boards both inside Unicamp and outside.

Ronei always conciliated his role as an international level researcher with his teaching and administrative activities at Unicamp. He never stopped actively collaborating in the various collegiate bodies that make up the administration of Unicamp (notably after his rise to the highest degree of an academic career, when he was approved for tender in the position of Full Professor, in 2013). He was also head of the Department of Analytical Chemistry at IQ-Unicamp on two occasions, and associate coordinator of the Post-Graduation in Chemistry Committee at that university. He was considered a talented and dedicated Professor by undergraduate and post-graduate students and was enormously respected (and liked, though he himself may never have realized it).

In his personal life, he was always a loyal, reserved and discreet colleague; in all aspects of his professional and personal life he acted impeccably ethically – even though it often failed to bring him any personal advantage (and on some occasions, just the opposite).

His dedication to teaching and research was unquestionable; however, he never became obsessed with research and showed extreme and sincere modesty. In particular, he always placed the well-being of his family (his wife, Ines, and his son, Pedro, as well as his parents) above all and he valued living with them like few others.

On April 25, 2020, Ronei Poppi suddenly left this world. The gap he left in Chemical Sciences in Brazil is only smaller than the gap that will be felt by his colleagues, friends, collaborators and students.



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ARTICLE

Stability of Vitamin C in Enriched Jelly

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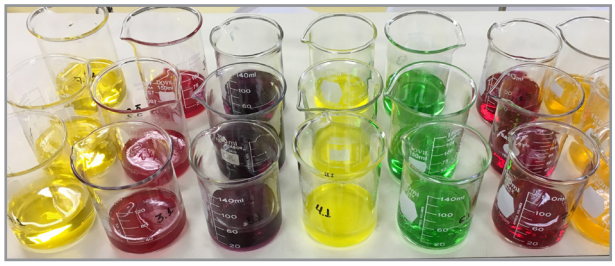

Fortification of foods with vitamins has become increasingly common. However, further studies on the stability of vitamins in foods are required because these compounds can easily degrade. The objective of this study was to evaluate the stability of ascorbic acid (AA; vitamin C) in fortified gelatin after dissolving the powder in water at room temperature (25 °C), after preparing the jelly according to label instructions, and after storing the ready-to-eat product for three days in the refrigerator, comparing the obtained values to those stated on the label. AA was measured by iodometry using an automatic potentiometric titrator with a platinum ring electrode. The AA contents of all the samples dissolved in cold water were either equal to or above those stated on their labels. However, the AA contents of two of the prepared and stored samples were below their stated label values, confirming AA degradation.

Keywords: Gelatin, vitamin, ascorbic acid, stability, potentiometry.

INTRODUCTION

Gelatin is a protein product derived from partial hydrolysis of animal collagen, which is present in bones and skin and is obtained primarily from pigs and cattle. It is extracted by acid or alkaline hydrolysis, then purified and concentrated [1]. All types of gelatin have similar compositions and contain water, a small amount of mineral salts, and connective tissue protein. However, depending on the raw material, type of pretreatment, and rate of hydrolysis, various types of gelatin, having different properties, can be obtained for different purposes. Gelatin is widely used in the food industry to improve the elasticity, consistency, and stability of food products. It is also used as a fat substitute, particularly in dairy products, to reduce the caloric contents of various foods without significantly affecting their taste [2]. Fruit-flavoured gelatin desserts are popular in Brazil. These products are easily prepared, inexpensive, and highly accepted by consumers of various age groups. Therefore, gelatin can be supplemented with micronutrients to provide more nutritious foods to consumers, in view of the inadequate intake of vitamin C by the Brazilian population [3]. Several industrialised foods, such as cookies, cakes, bread, and desserts, are fortified with vitamins to increase their nutritional, commercial, and market value.

Resolution RDC Nº 54/2012 of Brazilian Health Regulatory Agency of the Ministry of Health (ANVISA/MS) established that the use of complementary nutritional information, such as “vitamin source” and “vitamin rich”, on food labels is allowed, provided that the foods contain respectively, 15 or 30% of the

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recommended daily intake of the said micronutrient in 100 g or 100 mL of ready-to-eat product or serving [4]. Foods fortified with ascorbic acid (AA; vitamin C) have increased acceptance by consumers as there is scientific evidence supporting the benefits of consuming this micronutrient, including improvement of immune function, increased absorption of iron from the product, and/or antioxidant properties [5].

Different methods have been used for the determination of vitamin C in foods, including spectrophotometry, electrophoresis, voltammetry, titration, and high performance liquid chromatography (HPLC) [6-8]. The iodometric titration for vitamin C determination is the official method of Adolfo Lutz Institute, a Central Public Health Laboratory of Sao Paulo State. In this method, the iodine reacts with vitamin C, and the endpoint of the titration is determined by the first excess of iodine in the solution, that reacts with the starch indicator, forming a complex with an intense dark blue-violet color [9]. This method is single, fast, and reliable, however, the endpoint of the titration cannot be easily detected when the sample has intense color, such as gelatin. The alternative to excluding color interference was to transfer the traditional iodometric titration to automatic potentiometric titrator, as performed in this work, in which the endpoint of the titration is indicated by platinum ring electrode, and no color interference occurs.

Since iodine solution (I_2) is highly unstable to be used as a titrant, the present method is based on the reaction of potassium iodide (KI) with potassium iodate (KIO_3) titrant solution, in acidic medium (H_2SO_4) releasing I_2 (Equation 1) which reacts with AA (Equation 2) [9].

$$5KI + KIO_3 + 3H_2SO_4 \rightarrow 3I_2 + 3K_2SO_4 + 3H_2O \qquad \text{(Equation 1)}$$

$$C_6H_8O_6\ (AA) + I_2 \rightarrow C_6H_6O_6 + 2HI \qquad \text{(Equation 2)}$$

Several physical and chemical factors can affect the stability of vitamins, including temperature, humidity, oxygen, light, pH, oxidizing and reducing agents, presence of metal ions, and/or other ingredients in the matrix [10]. Since AA is highly unstable, it is crucial to determine its concentration during food preparation and storage, especially in gelatin products, which involves heating during preparation.

The objective of this study was to evaluate the stability of AA-fortified gelatin by determining the AA content after dissolving the powder in cold water, immediately after preparation according to the manufacturer's instructions, and after storing the ready-to-eat product for three days in the refrigerator. An assessment was also made as to whether AA concentrations before and after storage agreed with the values stated on the nutritional information label.

MATERIALS AND METHODS

Samples

Eight gelatin powder samples containing nutritional information regarding fortification concentrations of AA were locally purchased in São Paulo, Brazil.

Standards and reagents

L-ascorbic acid (≥ 99.9%) were purchased from Sigma-Aldrich (St Louis, MO, USA). Analytical-grade reagents sulfuric acid (H_2SO_4), potassium iodide (KI), and potassium iodate (KIO_3) were purchased from Synth (Sao Paulo, Brazil).

Determination of AA

AA concentrations were evaluated at three stages: Stage 1) after dissolving the gelatin powder in water at room temperature (25 °C); Stage 2) immediately after preparation according to the manufacturer's instructions (95 ºC); and Stage 3) after storing the product in a refrigerator (4–6 ºC) for three days, which simulated domestic consumption and met the expiration date recommendations described on the package label. AA concentrations were determined by iodometry using an automatic potentiometric titrator with a Tiamo® software-controlled platinum ring electrode (Metrohm Pensalab, Herisau, Switzerland) [6]. For

each sample, the gelatin powder from the same package (stages 1, 2, and 3) equivalent to 5–10 mg of AA content was weighed in a 150 mL beaker. Samples of stage 1 analysis were dissolved in water at room temperature (25 °C), while samples of stage 2 and 3 were first dissolved in water at 95 ºC, and then cold water was added, proportionally, according to method of preparation on the label. Stage 1 and 2 analyses were performed as soon as the dissolution was complete, and stage 3 analysis, after 3 days stored in a refrigerator. For the titration procedure, 10 mL of 20% (v/v) sulfuric acid (H_2SO_4) and 1.0 mL of 10% (v/v) potassium iodide (KI) were added to the beaker, and the sample was titrated with 0.002 M potassium iodate (KIO_3). Each mL of the KIO_3 solution used in the titration was equivalent to 0.8806 mg of AA. The data was transferred to Excel spreadsheets, and the results were analysed using Tiamo Software and expressed in mg of AA per serving.

Validation of the titrimetric method for vitamin C was carried out according to the guidelines of the International Conference on Harmonisation (ICH) [11]. For the gelatin matrix, the recovery test was performed using recovered standards of AA spiked in gelatin at three concentration levels and three replicates.

A standard AA solution (concentration = 1.0 mg mL^{-1}) was used as an internal control. Titrations with 10 mL of this solution were performed in triplicate. Resulting AA contents of 10 ± 0.15 mg indicated that the performance of the method is satisfactory.

Data analysis

The results were expressed in terms of means and standard deviations (n=3). The one-way analysis of variance (ANOVA) and Tukey's multiple comparison test was used to differentiate between the means of the vitamin C content ($p < 0.05$) determined in three steps. All statistical analyses were conducted using Microsoft Excel for Windows® 10 (Microsoft Corporation, Redmond, WA, USA, 2010) and Action Software (Estatcamp, 2014). The level of statistical significance was set at 5% for all analyses [12].

RESULTS AND DISCUSSION

Vitamin C stability

The validation parameters for titrimetric method for determination of vitamin C are reported in Abe-Matsumoto et al [13]. The LOD and LOQ is 1.0 mg and 3.0 mg, respectively [13]. Recovery (%) for the gelatin matrix ranged from 97.2% to 100.7%, where the results (%) of triplicate for each level (1, 2 and 3) were respectively 98.5 ± 1.9, 99.2 ± 0.5, and 99.2 ± 0.6, and was considered satisfactory according to ICH [11].

The AA concentrations stated on the nutritional information labels of the samples ranged from 8.1 to 16.0 mg per 120 g of product. Resolution RDC Nº 360/2003 of ANVISA/MS allows a difference of up to 20% of the value stated on the label [14]. AA concentrations in the powder samples dissolved in water at room temperature (25 °C) were either below or equal to 20% tolerance allowed by the legislation (samples D and E) or above this limit (samples A, B, C, F, G, and H), indicating that the manufacturers fortified the products. After preparation according to the manufacturer's instructions, AA was highly degraded in two of the samples (C and D). After refrigerating the products for three days, AA was significantly degraded in three of the samples (A, C, and D), with the concentrations in two of these samples (C and D) were below those stated on their labels, and four of the samples (A, F, G, and H) had concentrations above 20% tolerance limit.

AA is easily oxidized even when stored in a refrigerator, which decreases its nutritional value. Phillips et al. [15] found that the loss of AA content in vegetable samples frozen for 12 months at -60 ºC ranged from 13.7 to 26.0%. However, AA was not degraded during the storage of tangerine juice under the same conditions, probably because of the high acidity of this fruit contributing to the compound's stability [15]. Antioxidant vitamins found in supplements, including vitamin C, were highly degraded in 90% of the evaluated samples stored for 12 months [16].

Although the preparation of gelatin involves heating, in the present study vitamin C was stable for most of the samples in comparison to other stability studies in the literature [15,16]. After 3 days of storage, only

two samples (C and D) showed vitamin C concentration below that declared on the label. In these samples, the manufacturer did not practice over-fortification to prevent degradation during preparation and storage, since the levels of vitamin C in stage 1 were close to that stated on the label. On the other hand, sample A, despite showing significant degradation after 3 days of storage, vitamin C content remained above the declared value, probably because in this case, the manufacturer practice over-fortification. This could be verified because the vitamin C concentration in stage 1 was about 50% above the declared value (Table I).

Table I. Ascorbic acid concentrations (mg per serving) stated on the nutritional information labels with their respective minimum and maximum tolerance ranges (± 20%) allowed by law and ascorbic acid contents of the gelatin samples dissolved in cold (stage 1), hot water (stage 2), and refrigerated for three days (stage 3).

Sample	Declared (acceptable range)	Cold water (Stage 1)	Hot water (Stage 2)	Stored for 3 days in the refrigerator (Stage 3)
A	8.9 (7.1–10.7)	13.79 ± 0.85[a]	13.65 ± 0.79[a]	11.50 ± 0.01[b]
B	10.0 (8.0–12.0)	12.25 ± 0.97[a]	11.32 ± 1.23[a]	10.64 ± 0.32[a]
C	8.1 (6.5–9.7)	11.33 ± 0.58[a]	6.22 ± 0.47[b]	4.71 ± 0.70[b]
D	8.1 (6.5–9.7)	8.80 ± 0.37[a]	5.82 ± 0.31[b]	5.41 ± 0.65[b]
E	10 (8.0–12.0)	11.35 ± 0.61[a]	10.34 ± 0.13[a]	9.05 ± 0.83[a]
F	16 (12.8–19.2)	24.65 ± 1.84[a]	20.48 ± 0.74[a]	19.63 ± 3.23[a]
G	16 (12.8–19.2)	22.68 ± 4.01[a]	22.01 ± 3.73[a]	20.83 ± 0.40[a]
H	8.9 (7.1–10.7)	12.56 ± 0.72[a]	11.55 ± 2.13[a]	11.31 ± 0.86[a]

[a and b] Means with the same letters for each sample were not significantly different from each other using the Tukey's test at a significance level of 5%.

Several intrinsic and extrinsic factors can affect the stability of vitamin C such as pH, food matrix composition, ascorbic acid concentration, temperature, and oxygen accessibility. The study of the influence of stability of vitamin C in apple and carrot purée, considering these factors, showed that extrinsic factors such as oxygen and temperature had the greatest impact on vitamin C stability. However, for the other products, the stability may depend on the food matrix composition [10].

The presence of malic acid as an acidifier in all samples may have contributed to the stability of vitamin C since this micronutrient is more stable in an acid medium [15]. Samples C and D, despite the presence of malic acid, also presented the anti-humectant tricalcium phosphate in the list of ingredients, which may have interfered with the acidity of the product, making vitamin C more unstable.

The enrichment of foods with vitamins is becoming increasingly common practice to improve their nutritional value. The enrichment process must be careful, as some micronutrients, especially vitamin C, can be easily degraded. Once the enrichment with vitamins is declared on the label, these products must follow the current legislation in relation to the declared and analyzed levels. Resolution RDC Nº 360/2003 of ANVISA/MS establishes that, for products containing micronutrients in an amount higher than the established tolerance (20%), the responsible company must keep available the studies that justify such variation [14]. In the case of gelatins, the manufacturer could over-fortify vitamin C, if degradation during preparation and storage could be justified. The values of vitamins declared on the label must be in accordance with the values analyzed in food prepared for consumption. Resolution RDC Nº 54/2012 of ANVISA/MS, a Technical Regulation on Complementary Nutrition Information, establishes the conditions for the use of the "Source of vitamins" or "Rich in vitamins" attributes, based on the percentage of daily reference intake (DRI) of the nutrient in 100 mL or 100 g of finished product or in the portion, that is, the declared nutrient content must be in accordance with that contained in the product ready for consumption. That is why the importance of analyzing vitamin C after the preparation and storage of gelatin, as this is

how the population will consume the product.

The Ordinance Nº 31/1998 of Health Surveillance Secretariat of the Brazilian Ministry of Health (SVS/MS) also allows nutrient over-fortification provided this is justified to guarantee the maintenance of the concentration specified on the label [17]. Considering that the analysed products were within shelf life, over-fortification may have been used to maintain the AA levels present until the end of shelf life. In samples that underwent degradation, the manufacturer most likely did not overdose. Due to this, after product preparation and storage, the AA concentrations were below the values stated on the label.

CONCLUSIONS

All the evaluated gelatin samples were fortified with AA. However, the AA concentrations in 25% of the samples prepared as recommended and stored for three days were below their declared values. Products having low AA concentrations cannot be labeled with “Source of Vitamin C.” In most of the samples, micronutrient overdose may have been performed to maintain the AA concentration stated on the label until the expiration date. The increasing supply of fortified foods in the Brazilian market warrants the need for constant monitoring of these products to ensure that the information available to consumers pertaining to vitamin concentrations in these products is reliable.

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ARTICLE

Use of Mobile Gas Chromatograph Coupled to Mass Spectrometer to Detect Toxic Compounds in Environmental Samples

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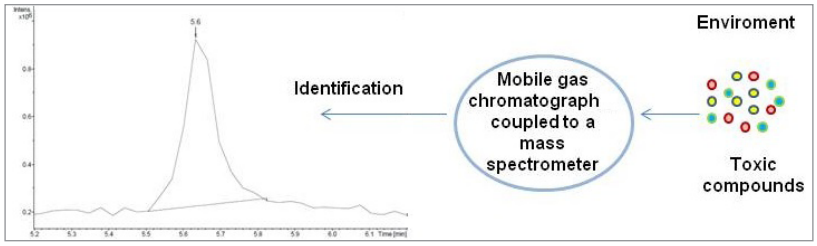

Chemical warfare agents are substances that can be used with military purpose for their ability to cause death, temporary incapacitation or permanent harm in the population. Identification of potentially toxic chemicals used as chemical weapons is of fundamental importance to ensure the physical integrity of the military and civilian population. The objective of this study was to test a method to detect the presence of chemical compounds in environmental samples through direct injection and using Tenax® tube connected to a mobile gas chromatograph coupled to a mass spectrometer (GC-MS) system. Three compounds from a chemical warfare list, used as precursors of chemical weapons, were chosen: 2,6-dimethylphenol, trimethyl phosphate and 1,4-thioxane. These compounds are commercially available for purchase, different from others representatives, which must be synthesized in microscale in a laboratory. The results obtained with the mobile GC-MS system were compared to those obtained with a bench top GC-MS system used in laboratory analysis. Results showed that the use of the mobile GC-MS system was adequate to identify the target compounds, highlighting the importance of its use in field analysis.

Keywords: Chemical weapons, Gas Chromatography, Mass Spectrometry, on-site analysis, mobile gas chromatograph-mass spectrometer.

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INTRODUCTION

According to the "Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and Their Destruction", toxic chemical compounds are those which may lead to death, temporary incapacity or permanent risk to humans or animals, regardless of their production method [1]. Since ancient times, chemical agents have been used as tools of warfare, however, the advent of the chemical industry in the second half of the nineteenth century has made its use technically feasible as weapons with great potential for mass destruction [2]. In the military context they cause more casualties than conventional weapons. A major difference between conventional and chemical weapons is the fact that chemical weapons target general population, not just military personnel on a battlefield. As such, it ceases to be an essentially military concern and becomes a social and economic concern.

Numerous techniques can be used to identify highly toxic chemical compounds with potential terrorist use. Among them, the chromatography, a physicochemical method of separating the components of a mixture, realized through the distribution of these components between two phases: one stationary and the other mobile [3]. Specifically, in the case of chemical warfare compounds, gas chromatography coupled to mass spectrometry (GC-MS) technique is the most widely used. The gas chromatography segregates the components of a mixture, while the mass spectrometry provides the structural information on each of them [4]. GC-MS analysis can also generate quantitative data when known concentration patterns are used with the unknown sample.

E^2M equipment (Bruker®) used in this study can be defined as a quadrupole mass spectrometer system aimed to be used for on-site analysis. Because of that it was developed to be a compact and robust system capable of be used statically or mounted on a vehicle. The system's greatest advantage is its sensitivity, since it is able of detecting compounds in concentrations on the order of parts per million (ppm). A feature of this system is the use of atmospheric air from the environment (78% nitrogen, 21% oxygen, 0.93% argon and 0.039% carbon dioxide) as a mobile phase, which makes the transport of mobile phase cylinders unnecessary [5]. On the other hand, the use of atmospheric air as a mobile phase would be a disadvantage in the analysis of easily oxidizable compounds. This made it necessary to use an inert gas as a mobile phase.

E^2M is a system that can be used for direct injection of samples or coupled to Tenax® tubes from which the retained analytes can be desorbed and introduced into the chromatographic column. The first technique used for standard samples identification was based on direct injection in the E^2M system. Injectors are used to introduce the sample into the GC column. This direct injection has a good accuracy, precision and can be used with a wide range of analyte concentrations. A small amount of liquid (microliters) is injected through a septum (using a special microliter syringe) into the hot GC injector. It is kept hot by a relatively large, metal heater block that is thermostatically controlled. The sample is immediately vaporized and a pressurized, inert, carrier gas – which is continually flowing from a gas regulator through the injector and into the GC column – sweeps the gaseous sample, solvent, analyte into the column. In this system, gaseous sample is transferred into the column, increasing separation capacity and compounds identification. The second technique used for standard samples identification was based on thermal desorption with Tenax® tube, during analysis of environmental samples. The use of the Tenax® tube consists of a desorption method in which volatile compounds are adsorbed in a Tenax® tube matrix. Thermal desorption sample tubes can be used either empty, for desorbing volatiles from materials or packed with sorbent for retaining vapour organic phase. Tenax® is an inert sorbent used for hydrophobic samples. Considering this, the main purpose of this study was to test a methodology for the detection of chemical compounds using a mobile equipment (Bruker®) simulating on-site analysis. For this purpose, samples were analyzed by GC injector and Tenax® cartridge and then compared to analysis made with a bench equipment (Agilent®). Development and validation of this methodology will make it possible to obtain a robust and reliable analysis of sample contaminated with toxic compounds, using a mobile equipment, resulting in a faster response in contaminated areas.

MATERIALS AND METHODS

Equipment

For this study, a Bruker® gas chromatograph coupled to mass spectrometer (GC-MS) system, model E²M, was used. Such equipment was developed for analysis of samples in the field, and can be transported. For this, it is a robust equipment.

Reagents

Three analytical standards were used: 2,6-dimethylphenol (Merck, #S4766472), trimethyl phosphate (Sigma-Aldrich, #MKBS5276V), 1,4-thioxane (Sigma-Aldrich, #MKBL9089V). The solvent used in the preparation of samples was methanol (Vetec, #DCBD2408V). For linear retention index (LRI) calculated based on alkane series, a saturated alkanes standard (C7-C30 from Sigma, #LC13543V) was used.

Sample preparation

For both direct injection and Tenax® tube assays, the chemical compounds were diluted in methanol. In direct injection, solutions were injected in the GC-MS systems using a syringe. For Tenax® tube, after sample preparation, tubes were disposed near the opened vial with the solution and air sample pumped ten times with an Accuro manual pump, Dräger®. Sample tubes of 100 mL were used.

Solutions

Solutions were prepared using methanol as solvent, following the description in Table I.

Table I. Concentrations of work solutions of reference chemicals used for direct analysis (mobile or bench top GC-MS systems) and Tenax® tube

	Work solution concentration (ppm)		
Reference chemical	**Direct Analyses**	**Bench top**	**Tenax® tube**
2,6-dimethylphenol	20; 50; 75; 100; 125; 150; 200	10; 15; 20; 30; 40	50; 75; 100; 150; 200
Trimethylphosphate	300; 500; 750; 1000; 1500; 2000; 3000	10; 15; 20; 30; 40	500; 750; 1000; 1500; 3000
1,4-thioxane	50; 100; 150; 200; 250; 300; 350	2.5; 5; 7.5; 10; 12.5	50; 100; 150; 300; 350
Compound mixture (2,6-dimethylphenol; Trimethylphosphate; 1,4-thioxane)	1000	—	—

Chromatographic conditions

The chromatographic column used for direct injection in the mobile GC (E²M-Bruker®) was a MXT-5 column (Restek) of 12 m, internal diameter of 0.32 mm and film thickness 0.5 µm; the injector temperature was 240 ºC; the initial oven temperature was 45 ºC held for 1 minute, followed by an increase of 15 ºC per minute up to 160 ºC held for 1 minute and, finally, an increase of 35 ºC per minute up to 240 ºC held for 3 minutes. The mobile phase was atmospheric air with flow rate of 1.5 mL/min.

In direct injection in the bench GC (Agilent®), a DB5-MS column of 30 m, internal diameter of 0.25 mm and film thickness 0.25 µm was used; the injector temperature was 250 ºC; the initial oven temperature was 40 ºC held for 1 minute, followed by an increase of 10 ºC per minute to 300 ºC held for 10 minute. The mobile phase was ultra-pure helium with flow rate of 1mL/min.

For Tenax® tube, the chromatographic column used was a MXT-5 column of 12 m, internal diameter of

0.32 mm and film thickness 0.5 µm; the injector temperature was 240 ºC; the initial oven temperature was 45 °C for 1 minute, followed by an increase of 15 °C per minute until 160 ºC held for 1 minute, and finally an increase of 35 ºC per minute up to 240 ºC, held for 3 minutes. The mobile phase was atmospheric air with flow rate of 1.5 mL/min.

Data analysis

The mass spectra were obtained in the range of 15–600 *m/z*. The identification of chemical agents was performed using the OPCW Central Analytical Database library and the comparison was performed by the AMDIS software.

Calibration curves were constructed according to the ANVISA's Resolution RDC 166/2017 [6], which defines that 3 curves are obtained in graphic signal intensity as a function of the concentration, and at least 5 different concentrations should be used. For each analytical standard, 5 concentrations were analyzed and plotted on a graph as described. Then, the equation of the line and r^2 were determined with the aid of the LibreOffice Calc application. In order to prove linearity, the value of r^2 must be greater than 0.99 [6]. Also, according to the ANVISA's Resolution, the calculation of the limit of detection (LD) is given by Equation 1:

$$LD = \frac{3.3 \times \sigma}{IC} \qquad \text{Equation 1}$$

where σ is the standard deviation of the intercept with the Y axis of at least 3 calibration curves constructed with concentrations close to the supposed limit of detection and IC is the slope of the line obtained in the calibration curve.

To calculate the LRI based on saturated alkanes standard (C7-C30) Equation 2 was used:

$$RI = (N \times 100) + [2 \times 100 \left(\frac{t_c - t_n}{t_{n+2} - t_n}\right)] \qquad \text{Equation 2}$$

where RI is retention index; N is the number of carbons of the previous hydrocarbon; t_c is the retention time of the compound of interest; t_{n+2} is the retention time of the posterior hydrocarbon; t_n is the retention time of the previous hydrocarbon; n+2 is used to calculate retention index, considering that OCAD library data were obtained using saturated alkanes standard with even carbon numbers so, data must consider only even alkanes with even carbon number [7].

The alkane series standard was injected (1 µL) into the GC-MS system operating under the conditions previously described, and their respective retention times were used as an external reference standard for calculating the RI, together with the retention times of each compound of interest. Otherwise, it represents an important tool of identification and differentiation of isomer compounds.

RESULTS AND DISCUSSION

Analysis and determination of detection limit for 3 toxic compounds (2,6-dimethylphenol, 1,4-thioxane and trimethyl phosphate) was done using GC injector in E^2M GC-MS equipment. Such procedure was tested for each compound of interest in order to determine the limit of detection individually. Only this way would be possible to determine limitations and capabilities of this equipment and method. Otherwise, limit of detection could be used as an important tool for analysts and technicians that operate mobile laboratories or first responder teams against accidents or attacks involving chemical warfare agents or toxic industrial compounds.

For this step, three analytical standards were used: 2,6-dimethylphenol, trimethyl phosphate and 1,4-thioxane. For each compound it was verified the retention time and mass spectra, as well as a calibration curve to study linearity and limit of detection according to ANVISA RDC 166/2017 [6].

The analysis of 2,6-dimethylphenol allowed to define total ion chromatogram and its retention time as 5.6 minutes (Figure 1A), as well as to determine the mass spectrum obtained in our experiments (Figure 1B). This spectrum was compared to the OCAD spectrum (Figure 1C), correctly identifying the chemical agent analyzed.

For limit of detection determination, a calibration curves mean was performed, achieving linearity requisition. The standard deviation of the points that intercept the Y axis was obtained using the software LibreOffice Calc, and its value was 10907,51. Substituting this value into the limit of detection equation (Equation 1), the calculated limit of detection for 2,6-dimethylphenol was 7.15 ppm.

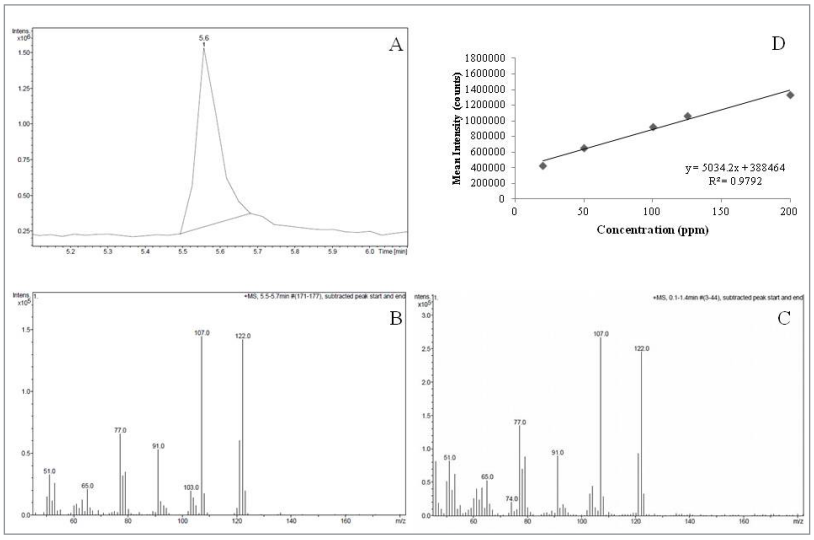

Figure 1. A: Total ion chromatogram obtained in the 2,6-dimethylphenol analysis; B,C: Mass spectra obtained by the validated 2,6-dimethylphenol method and the OCAD library; D: Calibration curves mean. Concentration: 200 ppm.

After this limit of detection determination, a saturated alkanes standard (C7-C30) was used to verify the performance of the GC-MS system and calculate the retention index (RI) of each compound in the sample. Calculated RI values were compared with values found in the literature for columns of the same polarity. The standard of these alkanes was injected (1 µL) into the GC-MS system operating under the conditions previously described, and their respective retention times were used as an external reference standard for the calculation of the RI, together with the retention times of each compound of interest [8].

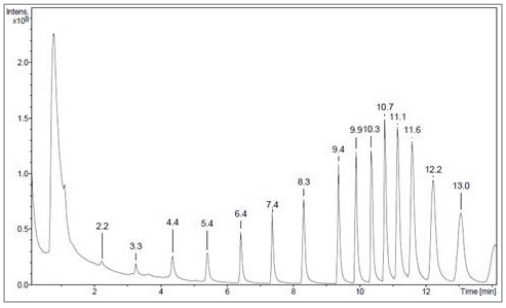

Figure 2. Total ion chromatogram obtained in the saturated alkanes standard (C7-C30) analysis.

As it can be observed, 2,6-dimethylphenol RT (OCAD libray) is 1.112, while LRI calculated, using Equation 2, was 1.120, a difference lower than 20 units between RI library and LRI calculated (D). It indicates a good performing of GC-MS system using MXT-5 column [8].

For the second compound analyzed, 1,4-thioxane, the retention time obtained was 3.2 minutes and its mass spectrum, both obtained and that one of the library, can be observed. As it can be verified in OCAD library, 1,4 thioxane RI is 897,743 while LRI calculated was 882, indicating a good performance of GC-MS system using the MXT-5 column. Following the limit of detection analyses, calibration curves were performed for 1,4-thioxane, as well as the curve obtained with the mean intensities, which can be observed in Figure 3.

In this case, the method meets the linearity criterion considering the mean of curve of the intensities. The standard deviation obtained with the measures of the points of intersection with the Y axis was 8223. Substituting this value into the equation for the calculation of the limit of detection results in 4.61 ppm.

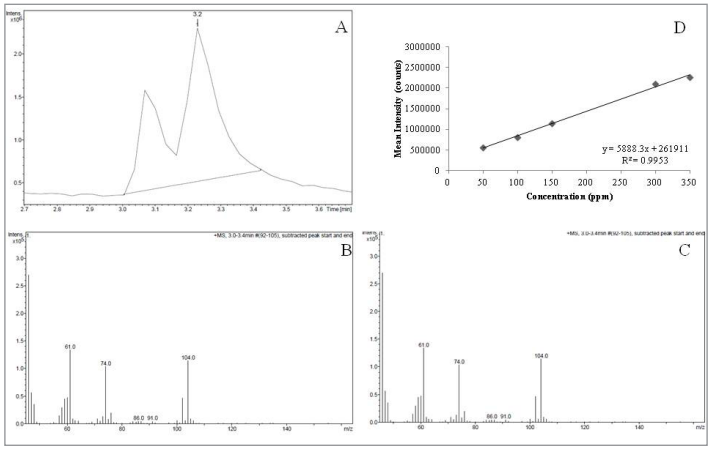

Figure 3. A: Total ion chromatogram obtained in 1,4-thioxane analysis; B,C: Mass spectra obtained by the validated 1,4-thioxane method and the OCAD library; D: Calibration curves mean. Concentration: 350 ppm.

Analysis of the third compound, trimethyl phosphate solutions, showed retention time 4.1 minutes. The ion chromatogram, mass spectra obtained and the OCAD library and mean intensity calibration curve are shown in Figure 4.

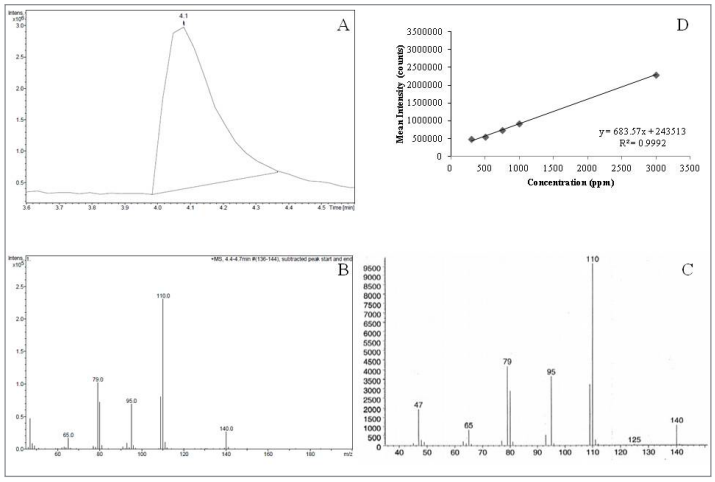

Figure 4. A: Total ion chromatogram obtained in trimethyl phosphate analysis; B,C: Mass spectra obtained by the validated method and the OCAD library; D: Calibration curves mean. Concentration: 3000 ppm.

As it can be observed in OCAD library, trimethyl phosphate RI is 946,1606 while LRI calculated was 972, indicating that for experimental condition used, it was not possible achieve a good chromatographic performance. The limit of detection was 49,19 ppm.

To check the performance of the mobile GC-MS when compared to a bench top equipment we decided to compare the obtained limits of detection with those that could be obtained on the Agilent equipment. We used the same reference chemicals and prepared solutions with the same solvent, but in different concentrations. Three calibration curves were obtained and they were used to obtain a calibration curve with the average of the intensities. Linearity and limit of detection were determined according to ANVISA RDC 166/2017 [6]. The analytical conditions are described in the experimental item.

The analysis of 2,6-dimethylphenol allowed to define its retention time as 10.232 minutes, according to Figure 5, as well as to define the mass spectrum obtained in our experiments. This spectrum was compared to the OCAD spectrum, correctly identifying the chemical agent analyzed (Figure 5).

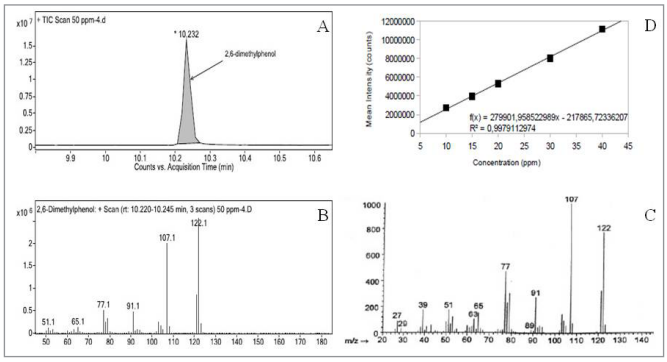

Figure 5. A: Total ion chromatogram obtained in the 2,6-dimethylphenol analysis; B,C: Mass spectra obtained by the validated 2,6-dimethylphenol method and the OCAD library; D: Calibration curves mean. Assay using a bench top equipment.

The standard deviation of the points that intercept the Y axis was obtained using the software LibreOffice Calc, and its value was 120263,35. Substituting this value into the limit of detection equation (Equation 1), the calculated limit of detection for 2,6-dimethylphenol was 1.41 ppm. As expected, the bench top instrument is more sensitive than the mobile one. However, difference between them is not so significant, considering that they are in the same order of magnitude.

For the second compound analyzed, 1,4-thioxane, the retention time obtained was 6.86 minutes. Figure 6 shows its mass spectrum, both obtained and that of the library, and the calibration curves performed following the limit of detection analysis, as well as the curve obtained with the mean intensities.

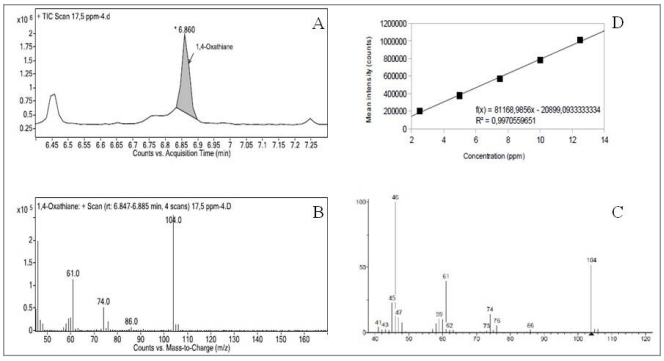

Figure 6. A: Total ion chromatogram obtained in the 1,4-thioxane analysis; B,C: Mass spectra obtained by the validated 1,4-thioxane method and the OCAD library; D: Calibration curves mean. Assay using a bench top equipment.

In this case, the method meets the linearity criterion in all obtained curves. The standard deviation obtained with the measures of the points of intersection with the Y axis was 29491,52. Substituting this value into the equation for the calculation of the limit of detection results in 1.20 ppm.

The third compound analyzed was trimethyl phosphate and its retention time was 7.493 minutes, according to Figure 7, as well as to define the mass spectrum obtained in our experiments. This spectrum was compared to the OCAD spectrum, correctly identifying the analyzed chemical agent.

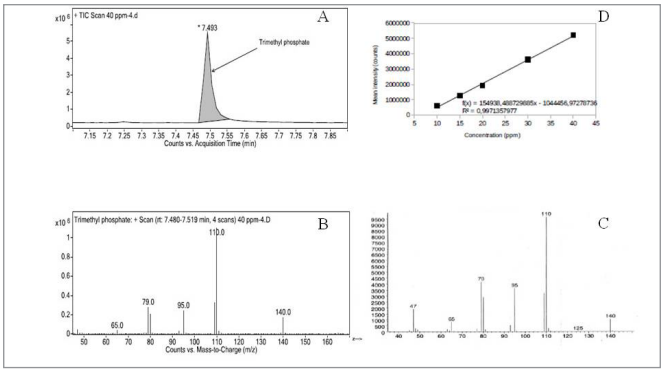

Figure 7. A: Total ion chromatogram obtained in the trimethyl phosphate analysis; B,C: Mass spectra obtained by the validated trimethyl phosphate method and the OCAD library; D: Calibration curves mean. Assay using bench top equipment.

In mean intensity curve the linearity criterion was met, including the curve with the average of the intensities. The standard deviation of the points that intersect the Y axis was 239491,59. Thus, the new limit of detection was 5.10 ppm. As expected, for all three compounds the bench top equipment showed lower limit of detection than the mobile equipment, but the difference between them is not so significant considering that they are all in the same order of magnitude.

Although the difference between both limit of detection in the bench top GC-MS and in the mobile equipment, linearity is better in the first one. Besides that, the repetition of the results is also better in the Agilent equipment.

These parameters could suggest that the E²M is not as good as the Agilent equipment. However, considering that we aimed a qualitative method to be used in the place where an accident or terrorist attack occurred, we could consider that our result is adequate to on-site analysis, that will be after confirmed by a forensic laboratory.

Last part of this study was evaluating limit of detection using Tenax® tube, a cartridge which adsorves environmental toxic molecules in air samples. Analysis and determination of limit of detection for three toxic compounds (2,6-dimethylphenol, 1,4-thioxane and trimethyl phosphate) were performed. Only this way would be possible to determine limitations and capabilities of this equipment and method using sample in a vapor state. For this step of the project, three analytical standards were used: 2,6- dimethylphenol, trimethyl phosphate and 1,4-thioxane.

The main advantage of this method is that it is not necessary to prepare a solution or use a solvent to extract the analytes from the matrix, considering that we can take the molecules directly from the air. Also, molecules will be concentrated in the Tenax® tube until saturation of the powder, so even if the concentration of the analyte is low, it can be concentrated before the analysis.

As a disadvantage, we can consider that it would be possible to analyze just volatile molecules, but, considering the CWA, most of them could be analyzed by this method, considering that they will be volatile at least partially.

The analysis of 2,6-dimethylphenol allowed to define its retention time as 5.6 minutes, according to Figure 8, as well as to define the mass spectrum obtained in our experiments. This spectrum was compared to the OCAD spectrum, correctly identifying the analyzed chemical agent. Following limit of

detection analysis, three calibration curves were performed for 2,6-dimethylphenol, as well as the curve obtained with the mean intensities, which can be observed in Figure 8.

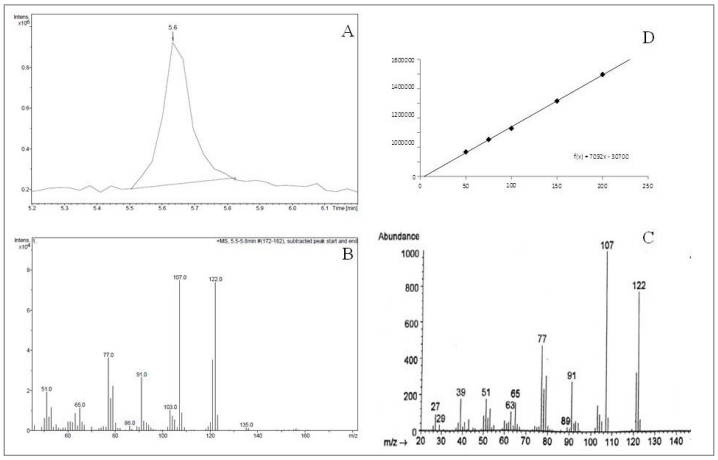

Figure 8. A: Total ion chromatogram obtained in the 2,6-dimethylphenol analysis; B,C: Mass spectra obtained by the validated 2,6-dimethylphenol method and the OCAD library; D: Calibration curves mean. Assay using Tenax® tube.

As can be observed in Figure 8, the linearity criterion was achieved using mean intensities. In view of this, the limit of detection was calculated using Equation 1 and the results were tested by analysing a solution with concentration near the calculated limit of detection. Considering that the standard deviation of the points that intercept the Y axis was obtained using the software LibreOffice Calc, and its value was 50320.06, limit of detection calculated is 23,41 ppm, a lower concentration (20 ppm) was tested. However, in this concentration, it was not possible to achieve a match greater than 80 (data not shown).

For the second compound analyzed, 1,4-thioxane, the retention time obtained was 3.1 minutes and its mass spectrum, both obtained and that of the library, can be observed in Figure 9. Following limit of detection analysis, three calibration curves were performed for 1,4-thioxane, as well as the curve obtained with the mean intensities, which can be observed in Figure 9.

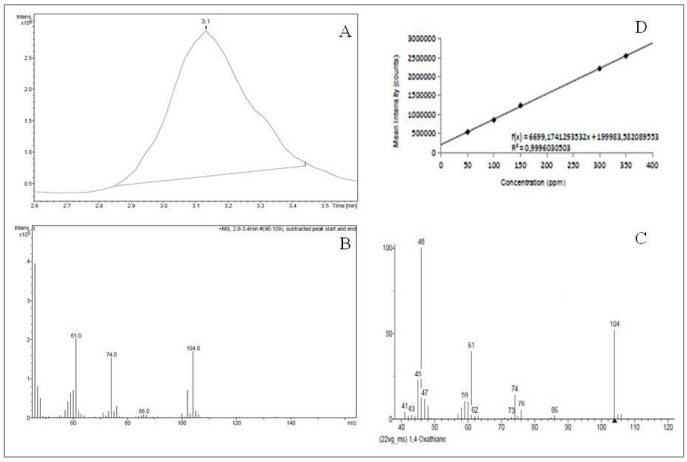

Figure 9. A: Total ion chromatogram obtained in the 1,4-thioxane analysis; B,C: Mass spectra obtained by the validated 1,4-thioxane method and the OCAD library; D: Calibration curves mean. Assay using Tenax® tube.

The mean intensities resulted in a linear curve. Also, the r² for all of them, are much better than for the 2,6-dimethylphenol. The standard deviation of the points that intercept the Y axis was obtained using the software LibreOffice Calc, and its value was 9005,85. Substituting this value into the limit of detection equation (Equation 1), the calculated limit of detection for l,4-thioxane was 4,43 ppm.

The third compound analyzed was trimethyl phosphate and its retention time was 4.5 minutes, according to Figure 10, as well as to define the mass spectrum obtained in our experiments. This spectrum was compared to the OCAD spectrum, correctly identifying the analyzed chemical agent (Figure 10). It was not possible to obtain calibration curve for this compound.

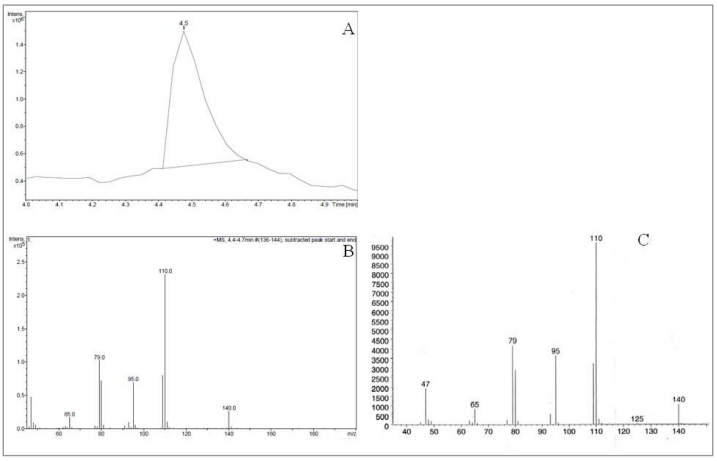

Figure 10. A: Total ion chromatogram obtained in trimethyl phosphate analysis; B,C: Mass spectra obtained by the validated , trimethyl phosphate method and the OCAD library; Assay using Tenax® tube.

Following limit of detection analysis, we tried to obtain three calibration curves for trimethyl phosphate, but that was not possible even for the mean intensities. Because of that, we could not calculate the limit of detection for trimethyl phosphate using the Tenax® tube.

Single stage thermal desorption – *i.e*., direct transfer of the analytes from the heated sample tube to the analytical system – produces broad component bands that are only compatible with packed column chromatography. A key advantage of tube monitoring methods is that many of the sorbents available do not retain water during the sampling process, thus preventing any risk of water interfering with the subsequent chromatographic analysis, especially in a GC-MS [9].

Using this methodology, it was possible to determine the minimum concentration detected in mobile GC-MS E²M Bruker®, but not for the trimethyl phosphate, whose linearity criterion was not met. Despite of the identification, we were not able to determine a linear curve using Tenax tube® for sample desorption. Probably, it was due to a small amount of vapor sample collected with the pump for each compound, although 10 pumping were carried out. It is worth noting that perhaps the most popular tube packing material – Tenax® TA – is a very weak adsorbent, suitable only for components less volatile than benzene.

Although it was not possible to determine a limit of detection using the mobile GC-MS E²M Bruker®, sample adsorption using Tenax® tube give enormous advantages over solvent extraction in terms of reusable tubes and environmental acceptability. Thermal desorption (TD) could replace solvent extraction for almost all air monitoring applications. A possibility to improve results is to use an automatic pump that would collect enough air volume until chemicals are concentrated in the Tenax® tube and then analyzed by GC-MS.

CONCLUSIONS

Gas chromatography combined with mass spectrometry (GC-MS) provides analytical information that is definitive for many types of samples containing organic analytes. Over the last decade, field-portable GC-MS systems have played a major role in key environmental as well as forensic applications [10].

Field analysis requirements typically include the need for rapid assessment of the volatile organic compounds (VOCs) present, because these compounds can be inhaled and, therefore, represent the highest immediate health danger. The VOCs that represent the most credible and immediate danger to individuals include many industrial compounds, such as phosgene or cyanogen chloride, as well as chemical warfare agents (CWAs), such as volatile nerve agent Sarin [10].

With all studied analytical method, it was possible to identify the chemical agents in relatively low concentrations, especially considering the lethal doses of each one, which are several orders of magnitude above the determined limits of detection.

Although we did not meet the linearity criterion in all cases, it is important to highlight that the objective was not to validate a quantitative method of analysis, but rather a qualitative method to identify such compounds in field analysis that will be later confirmed by forensic laboratories.

For these reasons, the proposed methods were considered adequate for their purpose, contributing to the qualification of the team and to the reliability of the results obtained by an equipment for its use in field analyses, especially those involving accidents and the need of care for victims.

Acknowledgment

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ARTICLE

Optimization of Extraction Induced by Emulsion Breaking Variables for Subsequent Determination of Crude Oil Salinity by Ion Chromatography

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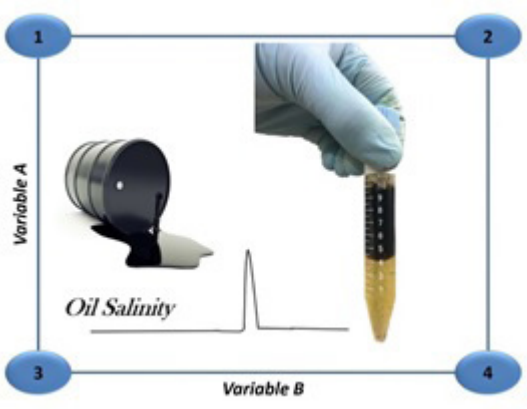

Due to natural geological oil formation and exploration processes, high amounts of saltwater are emulsified in oil, resulting in high salinity in oil extraction wells. This salinity is due to the presence of non-metals of forming inorganic salt, such as chloride, which, when subjected to high temperatures, tend to react with water vapor to form hydrochloric acid, causing distillation tower corrosion. In this context, extraction induced by emulsion breaking (EIEB) has been as an alternative procedure to the official ASTM D6470 method for chloride extraction and subsequent determination by ion chromatography in oil samples. Thus, the experimental EIEB variables of HNO_3 volume (V) and Triton X-114 mass (T) were optimized using a 2^2 factorial design with three central points. The optimal condition obtained for the EIEB and chloride determination was V = 500 µL and T = 0.5000 g. The developed procedure allowed for the assessment of samples presenting different °API (22.9 to 28.8), which originated from the post-salt. Besides, limits of detection of 0.3 – 0.4 mg kg^{-1} chloride were achieved. The accuracy of the procedure was confirmed by addition/recovery tests (100.4 – 100.7%).

Keywords: Chloride, Ion Chromatography, EIEB, Factorial Design, Corrosion, Refining

INTRODUCTION

Oil is a highly complex mixture consisting of saturated hydrocarbons, aromatics, and polycyclic compounds (resins and asphaltenes), as well as small amounts of organic compounds containing sulfur,

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nitrogen, oxygen and even lower amounts of metal compounds, particularly vanadium, nickel, iron, and copper [1-3]. Its chemical composition may vary from one specific site to another, according to regional and local variations, and the physicochemical processes that occur during its geological origin, thus leading to a wide variety of samples presenting different physicochemical properties [4,5]. Due to this, the determination of certain physicochemical characterization parameters such as density, viscosity, salinity, basic sediment and water contents (BSW); saturated, aromatics, resins and asphaltenes content (SARA), among others, is required to order to propose crude oil transportation and refining strategies [6-8].

Particular emphasis is given to salinity, as high amounts of saltwater are emulsified to the oil through natural oil geological formation processes and exploration and production processes, leading to high salinity values in oil extraction wells [3,9]. This salinity is due to the presence of non-metals that form inorganic salts, with chloride as the main salt-forming anion [9]. In parallel, salts contained in the oil, when subjected to high temperatures, tend to react with water vapor to form hydrochloric acid and, consequently, cause corrosion in oil distillation towers [9,10]. Thus, oil salinity determination should be performed to avoid potential problems during oil distillation and other oil production stages [11].

For the extraction of water in oil, there are several physical techniques, such as gravity or ultrasonic separation, skimming, absorption and filtration [12]. Extraction induced by emulsion breaking (EIEB) can be used for the extraction of emulsified saltwater in oil (aqueous extract), enabling the determination of chloride salts present in this extract. EIEB consists in the formation of oil-in-water emulsions by intense sample agitation (in this case, oil) mixed with an acidified surfactant. After heating, the emulsion ruptures, resulting in an organic phase containing the organic oil fraction and an acidified aqueous phase, the lower portion containing inorganic salts, termed the aqueous extract [13]. EIEB can be an advantageous proposition and an alternative method for the determination of oil chloride salts (salinity). Also, this method presents lower costs and is cleaner, due to the use of smaller sample volumes and organic solvents than the recommended oil salinity determination procedures (ASTM D 6470 [14] and ASTM D 3230 [15]). Besides that, chloride results after EIEB did not differ statistically from those obtained by the most commonly applied official method for the determination of this element in crude oil (ASTM D6470) [16].

Robaina et al. [16] applied the EIEB procedure to transfer the chloride to the aqueous oil phase during the emulsion breaking of oil samples. Chloride determination in the extracts was performed by ion chromatography (IC) using a conductivity detector. Several parameters were evaluated, such as the relation among the oil phase and aqueous phase, crude oil and mineral oil ratio, shaking time, type, and concentration of surfactant that could affect the performance of the method. However, no multivariate statistical procedure was used to evaluate the EIEB variables that could affect the chloride extraction to the aqueous phase and its determination by ion chromatography. Besides that, for extraction of chloride from samples was used mineral oil to solubilize the crude oil. Trevelin et al. [13] developed an analytical procedure for the determination of Ba, Ca, Mg, and Na in heavy oil samples after EIEB. Metal recovery percentages ranged from 99% to 104% and Ba and Na determination results showed good agreement with certified reference material (NIST 1634c) values.

In this context, the present study aimed to evaluate the use of a 2^2 factorial design with three central points to optimizer the variables of extraction induced by emulsion breaking (EIEB) for chloride extraction and subsequent determination by ion chromatography in oil samples. In addition, it is noteworthy that the EIEB was used to extract chloride from four oil samples in order to assess whether studied samples presented salinity exceeding the maximum permissible concentration for oil production refining and processing steps.

MATERIALS AND METHODS

Instrumentation

An ion chromatograph (883 Basic IC Plus, Metrohm, Switzerland) coupled to an autosampler (863 Compact Autosampler, Metrohm, Switzerland) was used for chloride determinations. The calibration curves ranged from 0.1 to 10.0 and 1.00 to 60.00 mg L^{-1} chloride. Conductivity signals were measured with a heated

DSP conductivity cell and chromatograms were acquired using the MagIC Net 3.1 software. Chloride ion separation was carried out using an analytical column (Metrosep A Supp 5, Metrohm, Switzerland), 150 mm in length with 5.0 µm particle size. A pre-column (Metrosep A Supp 5 Guard, Metrohm, Switzerland), 10 mm in length with 5.0 µm particle size, was used to protect the analytical column. A total of 20 µL were injected for all analyses. The parameters used to perform the analyses are listed in Table I.

Table I. Ion chromatograph operating conditions

Pressure (MPa)	10
Column temperature (°C)	25 ± 3
Injected volume (µL)	20
Time (min)	18

A mix stirrer (Phoenix, model AP 56), a heating plate (Centauro, CAMA-10), and a centrifuge (Edulab, model 80-2B) were used for the EIEB process.

Samples

Different oil samples (S1, S2, S3, and S4) were used, generating aqueous extracts E1, E2, E3, and E4, respectively. All samples were obtained from the Campos dos Goytacazes Basin, in the state of Rio de Janeiro, provided by the Petrobras S.A. Fluid Laboratory, located at the Imbetiba base in the city of Macaé, Rio de Janeiro. Table II presents performed physicochemical characterizations. The physical-chemical characterization parameters were carried out according to the procedure developed by Terra, Martins and, da Cruz (2019) [6].

Table II. Physical and chemical parameters determined in oil samples

Samples	$\rho_{24.2^{o}C}$ (g cm^{-3})[a]	$^{o}API_{24.2\,^{o}C}$ [b]	$^{o}API_{15.6\,^{o}C}$ [b]	µ (mPa s)[c]	BSW (% v v^{-1}) [d]
S1	0.8825 ± 0.0002	28.8	27.6 ± 0.1	53.3 ± 0.5	0.35
S2	0.8905 ± 0.0002	27.4	26.0 ± 0.1	34.8 ± 0.3	0.25
S3	0.9165 ± 0.0002	22.9	21.6 ± 0.1	127 ± 1	0.10
S4	0.9115 ± 0.0002	23.7	22.5 ± 0.1	304 ± 2	0.10

[a] $\rho_{24.2^{o}C}$ specific oil mass in g cm^{-3}, obtained at room temperature (24.2 ºC); [b] °API (*American Oil Institute*); [c] µ absolute viscosity determined in a timely and direct manner at room temperature of 24.2 ºC; [d] *BSW* (*Basic Sediment and Water*).

Material and reagents

Ultrapure water (resistivity = 18.2 MΩ cm) was prepared using a reverse osmosis system with ultraviolet disinfection (OS20LXE, Gehaka, Brazil). Chloride ion standard solutions were prepared by diluting a 1000 mg L^{-1} standard bromide, chloride, nitrate, sulfate, fluoride, and phosphate solution (SpecSol, Sao Paulo, Brazil) with ultrapure water.

Nitric acid 68% m m^{-1} P.A. (Vetec, Rio de Janeiro, Brazil), sulfuric acid 98% m m^{-1} P.A. (Dynamics, Sao Paulo, Brazil), sodium carbonate P.A. (Dynamics, Sao Paulo, Brazil), sodium P.A. (Dynamics, Sao Paulo, Brazil), sodium bicarbonate P.A. (Dynamics, São Paulo, Brazil) and Triton X-114 (Nuclear, Sao Paulo, Brazil) were used. Polypropylene tubes (Techno Plastic Products AG, Transadingen, Switzerland) (15.0 mL capacity) were used for the EIEB assessments.

Oil salinity determination

A mass of 3.0000 ± 0.0001 g of each sample was weighed directly into 15.0 mL polyethylene tubes. Then, 500 µL of concentrated HNO_3 and 0.5000 g of Triton X-114 (optimal conditions) were added to each polyethylene tube – Figure 1(a), which was then made up to 10 mL with deionized water. Subsequently, the tubes were shaken vigorously for 15 minutes using a mix stirrer to form oil/water emulsions. Breaking of the formed oil/water emulsions was achieved by heating for 15 minutes at 80 ºC using a water bath. The tubes were then centrifuged for 5 minutes at 3,000 rpm forming two phases, one aqueous containing the extracted chloride and one containing the organic oil portion – Figure 1(b). Finally, a thin-tipped pipette was used; inserting it through the organic phase of oil into the aqueous phase, where the entire aqueous phase formed was removed and weighed. The organic phase was discarded.

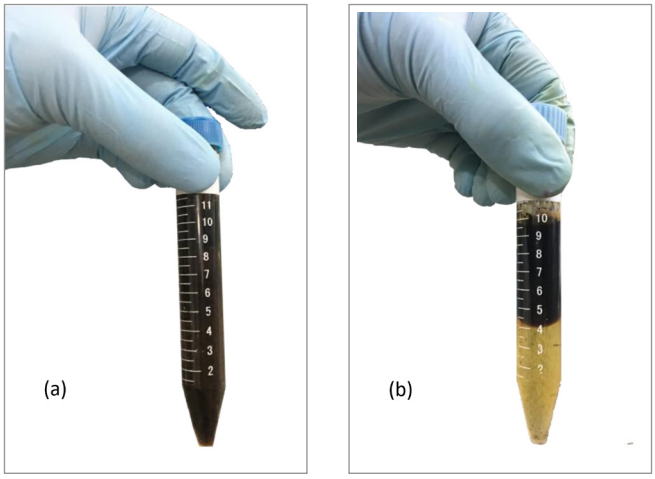

Figure 1. (a) Oil/water emulsion and (b) emulsion breaking (organic phase and aqueous extract E1).

Subsequently, the aqueous extracts were filtered through 0.45 µm cellulose acetate membranes (Filtrilo, Brazil) and diluted 10 times before being injected into the ion chromatography for chloride determination. Oil salinity was reported as mg kg^{-1} NaCl. Preparation blanks of each sample were also analyzed to assess the presence of chloride in water or reagents.

Due to the absence of certified material for oil extract samples, procedure accuracy was verified by chloride addition/recovery tests prior to EIEB. Concerning the recovery tests, a sodium chloride mass (before EIEB) was added to the S1 oil sample to obtain a final concentration of 833 mg kg^{-1} NaCl. Addition/recovery tests aided to ensure the efficiency of the proposed procedure.

Chromatographic conditions

An isocratic method (3.2 mmol L^{-1} Na_2CO_3 and 1.0 mmol L^{-1} $NaHCO_3$) at a flow rate of 0.7 mL min^{-1} was used for chloride separation during the injection stages of the standards for 18 minutes. The chloride peak appeared at 5.610 ± 0.020 min (Figure 2). Sulfuric acid at 0.100 mol L^{-1} was used as a suppressor. Between the injection of each sample, a blank consisting of ultrapure water was injected to clean the column. All aqueous extract (E1 – E4) analyzes were performed in duplicates.

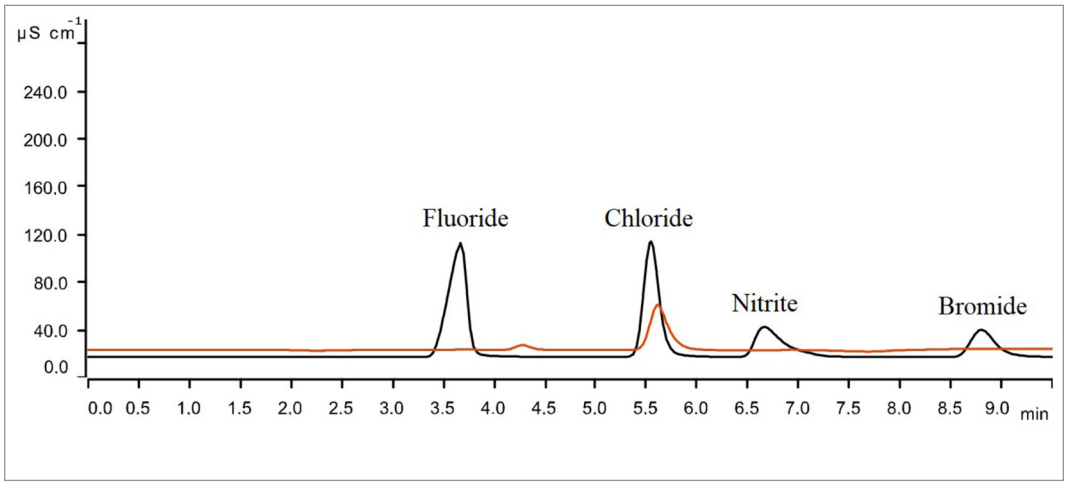

Figure 2. Typical chromatograms of the aqueous extract (E1) diluted 1:10 (red line) and a 60.0 mg L^{-1} chloride standard solution (black line).

EIEB Variable Optimization

A 2^2 factorial design with three central points was employed to evaluate the two EIEB variables of the emulsion - breaking extraction procedure: HNO_3 (V) volume and Triton X-114 (T) surfactant mass. A total of seven trials (2^k, k being the number of variables studied in the full factorial design, in this case, $2^2 = 4$; plus three trials at the central point) were performed. The entire optimizing process was performed using Microsoft Excel® 2010 software.

RESULTS AND DISCUSSION

Optimal EIEB conditions

In order to establish the best conditions for chloride extraction from the aqueous oil phase, a 2^2 factorial design with three central points was employed, evaluating two EIEB variables: HNO_3 (V) volume and Triton X-114 (T) mass. To avoid biased results the experiments were performed randomly. Table III presents the two variables (V and T) and the three studied levels (-1, 0, 1). All factorial design step was performed with oil sample S1.

Table III. Variables and levels assessed in the 2^2 Factorial Design with three central points

Experiment (sample S1)	Variables		Oil mass (g)[b]	Aqueous extract mass (g) (E1)[c]	Response (mg kg^{-1})[d]
	HNO_3 volume (µL) (V)[a]	Triton X-114 mass (g) (T)[a]			
1	500 (-1)	0.1225 (-1)	3.0253	5.9504	602.4
2	1500 (1)	0.1274 (-1)	3.0127	6.3159	461.7
3	500 (-1)	0.9125 (1)	3.1534	4.2130	478.0
4	1500 (1)	0.8901 (1)	2.9987	5.1196	369.4
5	1000 (0)	0.5362 (0)	3.0153	5.1049	506.9
6	1000 (0)	0.5130 (0)	2.9555	5.0055	513.1
7	1000 (0)	0.5326 (0)	2.9426	4.9038	493.3

[a]Values within the parentheses indicate the assessed levels; [b]Oil mass (S1) used in each experiment; [c]aqueous extract mass (E1) obtained after each EIEB. [d]chloride concentration determined in the aqueous extract (E1), expressed as reported in mg kg^{-1} oil (S1).

All effects and their experimental errors were then calculated from the responses generated in the complete 2^2 factorial design with three central points. Significant effects were analyzed at 95% confidence by replication at the center point and the *t*-test with 2 degrees of freedom (*t* student = 4.303). The significance of each effect was calculated from the multiplication of *t* student's value of 4.303 by the estimate of the standard error of the effect [5,17]. Figure 3 presents the significant effects of the assessed variables for chloride determination by ion chromatography for sample S1.

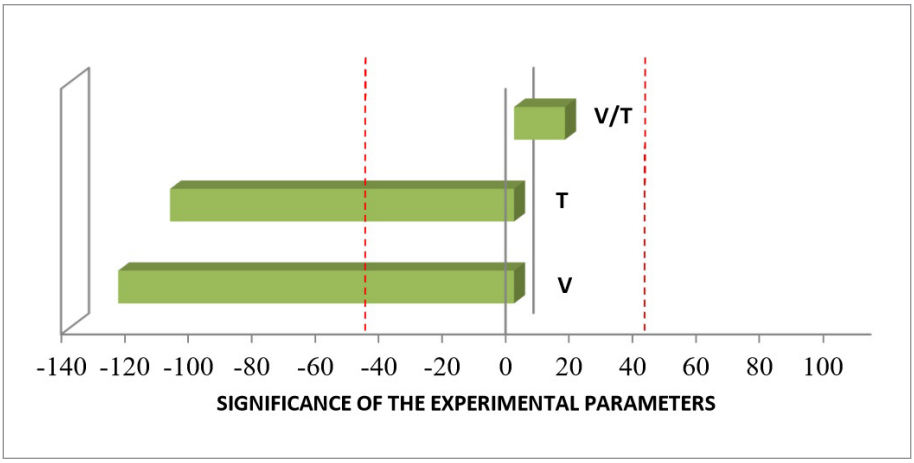

Figure 3. Graphical representation of the significance of the assessed variables: V (HNO_3 volume), T (Triton X-114 mass), and V/T (their interactions) for chloride determination in sample S1 (*t* student's value x standard error estimate = ± 43.6).

Variables V and T are significant for oil chloride extraction into the aqueous phase. Triton X-114 (T) is a surfactant used to reduce the surface and interfacial tensions of the medium and facilitate emulsion formation [13,18]. During emulsion formation, the two immiscible liquids (oil/water) are mixed under constant agitation, forming even droplets of one liquid inside the other [19,20]. This oil/water interaction allows inorganic chloride to come into contact with water droplets. During emulsion breaking, these droplets tend to stick together and the liquids separate again, allowing for the chloride to migrate to the aqueous phase. According to Figure 3, better results for chloride extraction would occur with lower Triton X-114 masses, that is, the increase in surfactant concentration decreased the extraction efficiency. Trevelin et al. [13] obtained a maximum extraction for the Ba, Ca, Mg, and Na elements when the surfactant was used at 5% m v^{-1} and observed a reduction in the extraction of these elements when were used lower Triton X-114 masses. Robaina et al. [16] used 2.5% m v^{-1} of Triton X-114 to the maximum extract of chloride in 0.5000 g of crude oil. Thus, Triton X-114 mass of 0.5000 g (5% m v^{-1}), center point, was used in this study to the maximum extract of chloride in 3.0000 g of crude oil, since a mass less than 0.5000 g of this surfactant can make it difficult to form the emulsion (due to the greater mass of crude oil used). In addition, as the V/T interaction was not significant, it is possible to optimize each variable independently and, therefore, only V (HNO_3 volume) was optimized, as it has a more significant effect during EIEB. The variable V (HNO_3 volume) was significant for chloride extraction from the oil sample. In addition, the 2^2 factorial design with three central points indicates that the HNO_3 volume should be decreased to obtain an optimal chloride extraction condition (Figure 3). In this sense, a univariate evaluation was performed, varying HNO_3 volume at five levels (700, 500, 300, 100, and 0 µL), to obtain the ideal volume of this acid for the EIEB (Figure 4).

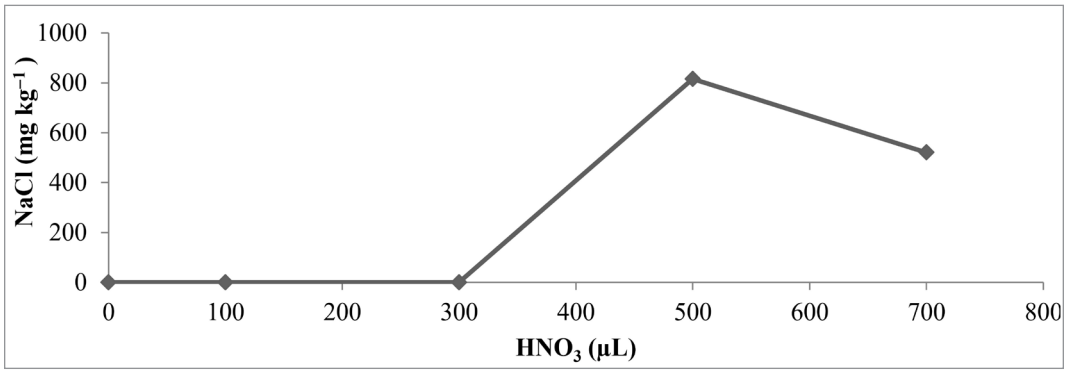

Figure 4. Variation of the extracted chloride to the aqueous phase in relation to the volume of nitric acid used in the extraction for sample S1.

Nitric acid aids in chloride extraction and provides greater stabilization of inorganic species in aqueous media, so that the analyte (chloride) does not precipitate and is not adsorbed to the vial walls [13]. EIEB only occurred at HNO_3 volumes of 500 and 700 µL. The use of the other volumes (300, 100, and 0 µL of HNO_3) did not result in phase separation, indicating that the presence of this acid is important for EIBE. Besides, decreased chloride extraction was observed when using 700 µL of HNO_3, indicating that a volume of over 500 µL is not required for chloride extraction. The high acidity resulting from HNO_3 may increase conductivity during chloride determination by ion chromatography, causing problems during this analysis. Therefore, although a high concentration of HNO_3 may aid chloride extraction, it may also impair its determination during ion chromatography analyses. Thus, V = 500 µL and T = 0.5000 g were used for the EIEB process applied to samples S1 – S4 to establish an ideal condition for chloride extraction and determination.

Oil salinity determination

After optimizing the optimum EIEB condition, chloride concentrations in the S1 – S4 oil samples were determined through chloride determinations in the aqueous extracts (E1 – E4). As chloride concentrations in aqueous extracts from S2, S3 and S4 were much lower than S1, two optimal working ranges (OWR) were obtained for chloride determination by ion chromatography, one with higher chloride concentrations and one with lower chloride concentrations. Table IV presents the performance characteristics of the procedure developed under the optimized extraction condition.

Table IV. Performance characteristics achieved after emulsion breaking induced extraction

Samples	OWR (mg L^{-1})	Linearity (r)	Sensitivity	LOD (mg kg^{-1})[b]	LOQ (mg kg^{-1})[c]	Conc (mg kg^{-1})[d]	Rec %
S1	1.0 – 60.0	0.995	0.296	0.3	1.0	829.9 ± 2.9	100.4
S1 rep[a]						827.2 ± 2.0	100.7
S2 – S3	0.1 – 10.0	0.999	0.232	0.4	1.3	ND	ND

[a]Duplicate of sample S1 used in the addition/recovery test; [b]LOD limit of detection; [c]LOQ limit of quantification; [d]Concentration recovered from 833 mg kg^{-1} addition of sodium chloride to oil sample S1 before EIBE. ND, not-determined.

Performance characteristics (linearity, LOD, LOQ, and recovery percentages) for chloride in sample S1 were established from the calibration curves. The concentration of the blank sample was 0.30 ± 0.03 mg kg^{-1}. The LOD was calculated as three times the standard deviation (s) of sample blank noise (s = 0.03 mg kg^{-1}) divided by the slope of the calibration curve (a), i.e. 3s/a, while the LOQ was calculated as 10 times the standard deviation (s) of sample blank noise (s = 0.03 mg kg^{-1}) divided by the slope of

the calibration curve (a), i.e. 10s/a, as defined by the International Union of Pure and Applied Chemistry (IUPAC). Linearity trends were assessed by the curve determination coefficient (r) ($r \geq 0.99$).

Recovery percentages (100.4 – 100.7%) were evaluated to verify the accuracy of the EIEB procedure, indicating a good accuracy (recommended range: 80 to 120%). The obtained concentrations were the result of two equipment determinations (duplicates) and two authentic duplicates (duplicates of the EIEB procedure).

Therefore, after defining the optimal EIEB conditions and performance characteristics, the EIEB process was performed for four oil samples (S1 – S4). Table V presents the chloride results in the aqueous extracts (E1 – E4) using ion chromatography.

Table V. Salinity results obtained (mg kg^{-1} NaCl oil) in oil samples (S1 – S4)

Sample	Oil mass (g)	Aqueous Extract Mass (g)	Chloride (mg L^{-1})[a]	NaCl (mg kg^{-1})
S1	3.0464	4.5666	333.3 ± 0.8[b]	824.6 ± 1.9[c]
	3.0489	4.8238	316.8 ± 0.5[b]	
S2	2.9600	3.6820	6.8 ± 0.1[b]	15.7 ± 2.6[c]
	3.0045	5.3150	6.0 ± 0.9[b]	
S3	2.9776	5.0511	6.94 ± 0.01[b]	16.8 ± 3.7[c]
	2.9262	5.1182	4.9 ± 0.1[b]	
S4	2.9699	4.9563	6.9 ± 0.1[b]	17.3 ± 2.3[c]
	2.9503	4.7013	5.95 ± 0.01[b]	

[a]Chloride concentrations in aqueous extracts (E1 – E4) determined in duplicate by the ion chromatograph. [b]Standard deviation of instrument duplicates. [c]Authentic duplicates of the EIBE procedure.

Samples S2, S3, and S4 presented lower sodium chloride concentrations, although above the LOQ (1.3 mg kg^{-1}), in the extracts (E2, E3, and E4, respectively), ensuring acceptable accuracy and precision. This control is essential, as the maximum salt content, expressed as the sodium chloride mass (mg) dissolved in 1 kg of oil is 570 mg kg^{-1} at the production stage, while refineries establish salt content of below 5 mg kg^{-1} [3,9]. Thus, salinity should be evaluated before refining for all assessed samples S1 – S4. In addition, sample S1 must undergo desalinization processes (NaCl removal) prior to the oil production and refining steps.

CONCLUSIONS

The screening step using a 2^2 factorial design with three central points allowed for the selection of the significant EIEB variables (HNO_3 – V volume and Triton X - 114 mass – T) for chloride extraction for the aqueous oil phase. The optimization of variable V (most significant) was performed in a univariate manner, to obtain the ideal volume of this acid for the EIEB process. High HNO_3 concentrations may facilitate chloride extraction into the aqueous phase. However, residual acidity in the aqueous phase may increase conductivity during chloride determination by ion chromatography, causing problems during the analysis. Interaction (V/T) was not significant for chloride extraction into the aqueous phase. Thus, variables V = 500 µL and T = 0.5000 g were established for the EIBE process.

The analytical procedure developed for chloride determination in the aqueous oil phase after EIBE displayed adequate precision and accuracy. Adequate linearity ($r > 0.99$), LOD (0.3 – 0.4 mg kg^{-1}) and LOQ (1.0 – 1.3 mg kg^{-1}) guaranteed method precision. Accuracy was confirmed by addition/recovery tests (100.4 – 100.7%). All samples displayed salinity values above the ideal maximum concentration for the oil

refining step (5 mg kg^{-1}). Besides, one of the studied samples presented salinity exceeding the maximum permissible concentration for oil production steps, of 570 mg kg^{-1}. Therefore, as the presence of chloride directly interferes in oil refining and processing, it should be assessed and determined in refineries as a means of obtaining new measures to prevent corrosion processes in the oil industry.

Acknowledgments

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FEATURE

PDF

2020 Pittcon Conference and Exposition was a success in Chicago

The 71st Pittcon was held from March 1 to 5 in McCormick Place, Chicago, and although the specter of the COVID-19 virus loomed and questions about the possible impact of the virus at that time remained largely unanswered, the conference still attracted a very engaged group and the exposition was a real achievement, although many international exhibitors and show attendees were unable to attend due to various government and personal travel restrictions.

Aerial view of the Pittcon 2020 Exposition – Photo Pittcon2020

The Wallace H. Coulter Lecture was presented by John A. Rogers, professor of Materials Science and Engineering, Biomedical Engineering and Medicine at Northwestern University, where he is also Director of the newly endowed Center for Bio-Integrated Electronics. The Wallace H. Coulter Lecture is a distinct feature of the annual Pittcon conference and exposition.

Professor John A. Rogers presenting the Wallace H. Coulter Lecture 2020 – Photo Pittcon2020

The 2020 Coulter Lecture was entitled “Soft, Skin-interfaced Microfluid Systems for Capture and Analysis of Sweat”. The topic follows Dr. Rogers’ research, which emphasizes such themes as nano-fabrication, techniques for unusual electronic and photonic devices, and bio-integrated and bio-inspired systems.

Dr. Ziva Cooper presenting the Plenary Lecture – Photo Pittcon2020

The 2020 Plenary Lecture 'Cannabis Constituents as Novel Strategies to Tackle the Opioid Epidemic' was delivered by Dr. Ziva Cooper, Research Director of the UCLA Cannabis Research Initiative in the Semel Institute for Neuroscience and Human Behavior and Department of Psychiatry and Biobehavioral Sciences. Dr. Cooper's research focuses on understanding the neurobiological, pharmacological, and behavioral variables that influence both the positive and negative potential of cannabis and cannabinoids. She has served on the National Academies of Sciences Committee on the Health Effects of Marijuana, serves on various editorial boards and is President of the International Study Group Investigating Drugs as Reinforcers.

The two above-mentioned lectures accentuated Pittcon 2020's 67 Short Courses, 34 Networking Sessions, and 1,575 Technical Program presentations. Many attendees took part in Pittcon 2020's technical programming and continuing education elements.

The 2020 Short Courses took place from 29th February – 5th March. With over 80 options to choose from and offered at beginner, intermediate and advanced levels, these range from one-half day up to two-days. There were a wide variety of classes covering relevant analytical topics, such as, food science, environmental, life science, pharmaceutical, among others. Courses for broad-based application and general lab functions included lab management, quality control, technical writing, statistics, data analysis and lab safety. Also, this year several new courses have been added to the schedule covering topics such as Raman spectroscopy and imaging, cannabis testing, chemometrics chromatography, sample preparation, multi-spectral imaging, and many more.

The exposition attracted 509 exhibitors occupying 925 booths, all displaying the latest innovations in laboratory science and laboratory technologies. The exposition hall, located at Chicago's McCormick Place convention center, was open March 3, 4, and 5, to a noteworthy 9,011 attendees. Exhibiting companies and attendees alike from numerous chemistry specialties within the bioanalytics, cannabis and hemp, energy, environmental, food science and agriculture, forensics and toxicology, industry and manufacturing, life science, nanotechnology and material science, and pharmaceutical fields.

Aerial view of the Pittcon 2020 Exposition – Photo Pittcon2020

The two 'Live Demo' areas on the exposition floor offered scheduled 15-20 minute interactive product demonstrations by leading exhibitors. These sessions also gave attendees an opportunity to engage

technical experts in question and answer sessions. The demos were open to all registered attendees.

In the Pittcon 2020 App, the official conference and exposition mobile app, attendees found valuable information to help plan and navigate the conference and exposition. It acted as an all-inclusive real-time show guide with details on exhibiting companies, technical sessions, Conferee Networking sessions, Short Courses, DemoZones, NEXUS Theaters, and much more.

Pittcon 2020 also marked the beginning of a new Pittcon tradition — the Pittcon Party. Held at Chicago's Museum of Science and Industry, the event attracted 1,250 guests and featured exclusive access to the museum, refreshments, music, dancing, and a stirring welcome speech from Pittcon 2020 President, Dr. Jane Chan.

The 'Pittsburgh Conference Achievement Award' at Pittcon 2020 was given to Professor Livia Schiavinato Eberlin, who is currently an Assistant Professor in the Department of Chemistry at The University of Texas at Austin. This award is presented annually to a researcher that made a significant and independent impact in an area of analytical chemistry, within the first ten years of their academic career. Prof. Eberlin was chosen based on her inventive research, strong collaboration, and development of diagnostic tools for cancer detection.

Professor Livia Schiavinato Eberlin winner of the 'Pittsburgh Conference Achievement Award'
Photo Pittcon2020

About Pittcon

Pittcon is the premier annual conference and exposition on laboratory science. This event not only covers analytical chemistry and spectroscopy, but also showcases developments made in the fields of food safety, environmental sciences, bioterrorism and pharmaceuticals.

Founded in 1950, Pittcon works in collaboration with the Spectroscopy Society of Pittsburgh (SSP) and the Society for Analytical Chemists of Pittsburgh (SACP) to assist in the development, research and future excellence of science education and its implementation.

Pittcon, a vital resource for knowledge, happens yearly to help keep you informed of, connected to and up-to-date on these significant ongoing findings and new instrumentation.

Pittcon 2021 will be held March 6 – 10, 2021, in New Orleans, Louisiana at the Ernest N. Morial Convention Center.

Sponsor Report

PDF

This section is dedicated for sponsor responsibility articles.

Unknown Profiling of Drinking Water Using High Resolution LC-MS/MS and New Software

Caroline Ding[1], Anastasia Kalli[1], Charles Yang[1], Tim Stratton[1], Hans Grensemann[2]

[1]Thermo Fisher Scientific, San Jose, CA, USA; [2]Thermo Fisher Scientific, Bremen, Germany

ABSTRACT

Purpose: Unknown compound profiling using high resolution LC-MS/MS and new software to confidently and quickly identify unknown compounds.

Methods: A treated tap water sample was collected from a city in China and stored in a plastic bottle before analysis. Mobile phase (5mM ammonium formate with 0.1% formic acid in water) was used as a blank to generate a data-dependent exclusion list for acquisition and background removal during data processing. LC-MS analysis was performed on the blank and water samples in positive modes with two replicate injections. The MS analysis employed a 70k HRMS full scan followed by top 10 data dependent ms2 collected on a Q Exactive mass spectrometer. Data analysis was performed with Thermo Scientific™ Compound Discoverer™ software using a single unknown data processing workflow.

Results: Data was processed using Compound Discoverer with one single workflow. The processing workflow included automatic unknown component detection, unknown elemental composition, library searching against mzCloud™ HRAM fragmentation library, ChemSpider database search, mass list search against built-in HRAM EFS library, automatic blank removal and structure interpretation using Custom Explanations and FISh Scoring on the fly. Batch searching against mzCloud online fragmentation library proved to be the most productive and confident way for unknown compound identifications. ChemSpider database search provided more hits which complements mzCloud search, however there were too many false positives from ChemSpider search. ChemSpider search using predicted formula helped reduce the number of false positives. Built-in FISh in Custom Explanations was used to verify hits from ChemSpider against MS2 data. All in all, Compound Discoverer software provides an effective and complete workflow for unknown identifications.

INTRODUCTION

Unknown compound profiling of water sample is very challenging due to complexity of contaminants in the water sample. Multiple software and lots of manual interpretations are usually required to identify the unknown compounds. New emerging software and tools shed light on unknown compound identifications. mzCloud is a new online HRAM fragmentation library which contains highly curated MS/MS and MSn spectra from different collision types and collision energies. It provides the fastest and most confident small molecule unknown compound ID. mzCloud search is integrated into Compound Discoverer 2.0 along with other tools like predicted compositions based on high resolution full ms, ChemSpider search that help partially identify the unknowns. This study demonstrates a simple yet powerful workflow for unknown compound profiling using high resolution Thermo Scientific™ Orbitrap™ mass spectrometer and Compound Discoverer software.

MATERIALS AND METHODS

Sample Preparation

Untreated tap water and mobile phase blank (injection volume 50 µL) were directly injected on to the column for chromatographic separation and MS analysis.

Analytical Method for LC-MS analysis

Chromatographic separation was performed with a Thermo Scientific™ Dionex™ Ultimate™ 3000 RS LC system using a Thermo Scientific™ Accucore AQ column (100 x 2.1 mm, 2.6 µ particle size). Mobile phase A was 5 mM ammonium formate and 0.1% F.A in water. Mobile phase B was 5 mM ammonium formate and 0.1% F.A in MeOH. Mass spectrometric analysis was performed on a Thermo Scientific™ Q Exactive™ Plus Orbitrap mass spectrometer operated in full MSddMS2 mode. Analysis was performed in positive ion mode followed by top10 data-dependent MS/MS scans. Resolution for the full MS scan was set at a 70,000 and at 17500 for the ddMS2 scans. Stepped collision energy was used at 20, 40 and 60. Analysis time, including column equilibration, was 25 min.

Retention time (min)	Flow (ml/min)	%B
0.00	0.300	2.0
0.50	0.300	2.0
2.00	0.300	40.0
20.00	0.300	95.0
22.00	0.300	95.0
22.10	0.300	2.0
25.00	0.300	2.0

Data Analysis

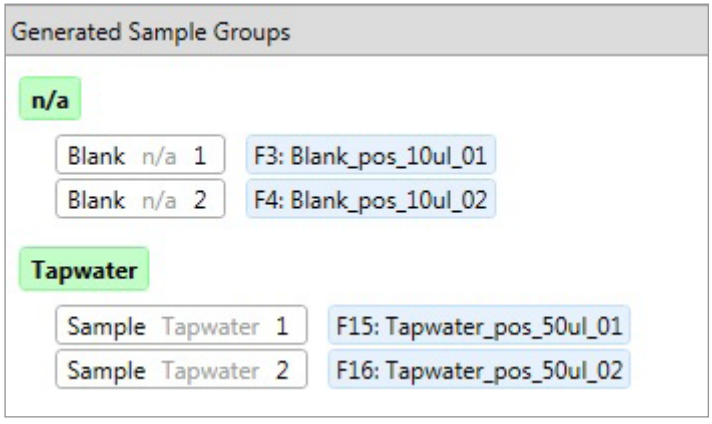

Figure 1. Sample grouping.

Samples and blanks were grouped based on user defined study factor and processed together. In this study the grouping was based on defined water type "TapWater" (see Figure 1). Sample grouping was persisted into data processing and results display.

The HRAM data was processed by Compound Discoverer software using a single processing workflow (Figure 2). The workflow employed unknown compound detection followed by online ChemSpider, mzCloud™ database search and local EFS HRAM compound database search. The Mark Background Compounds node hides the background compounds in the blank files from the result table.

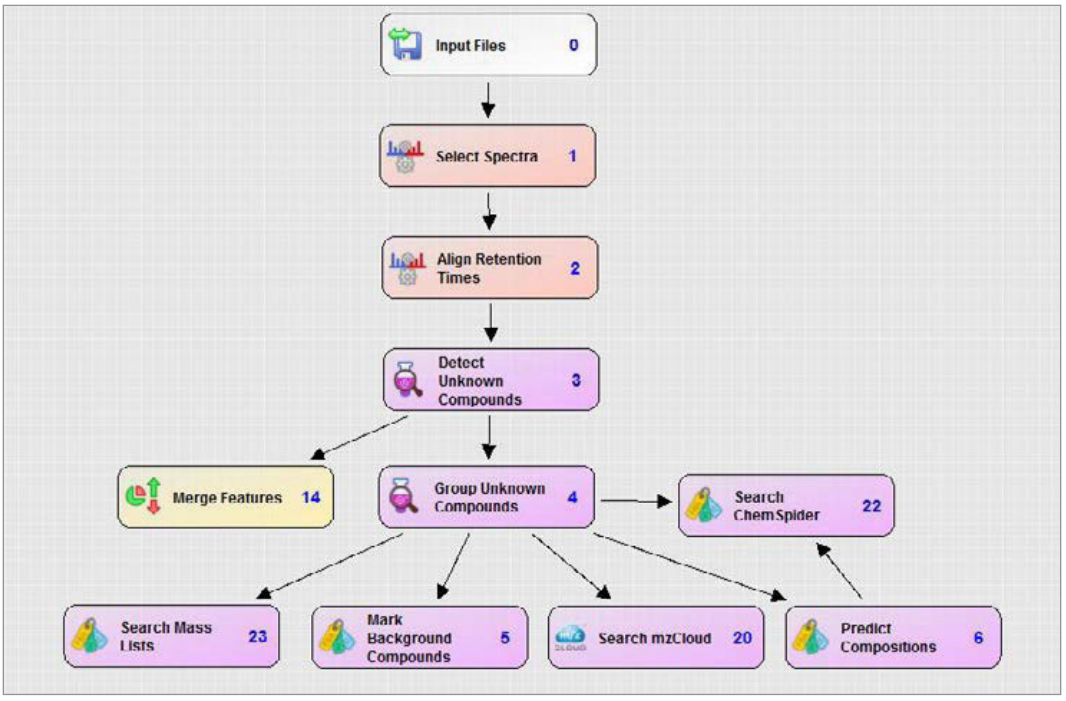

Figure 2. Workflow tree in Compound Discoverer software.

RESULTS

The results review in Compound Discoverer is broken into three parts: 1) Chromatogram view which interacts with the result table; 2) Mass Spectrum view which also interacts with the result table and displays the spectral tree for selected compound; 3) Result tables: the most important table is the Compounds table on the far left (See Figure 3). All the views can be docked, repositioned or dragged onto a second monitor.

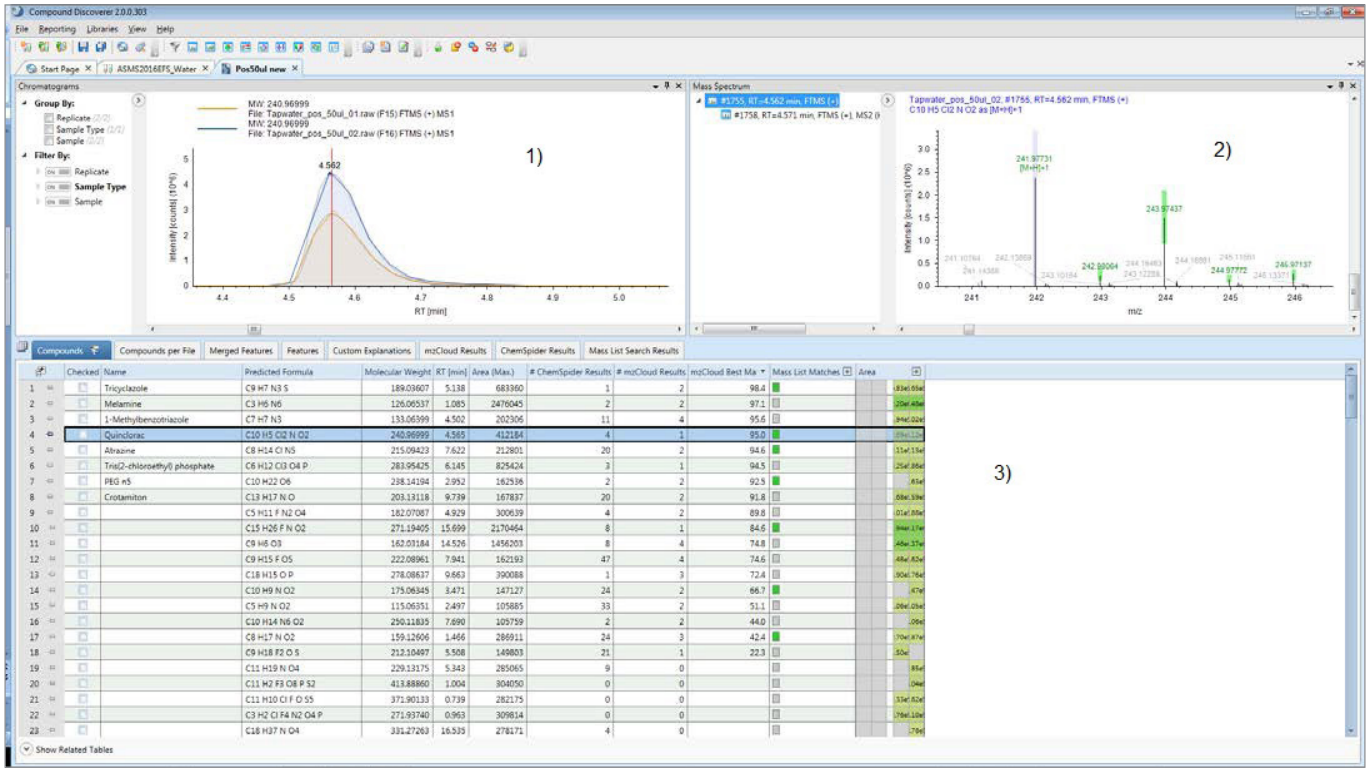

Figure 3. Result View in Compound Discoverer.

Result Filtering

185 compounds with unique molecular weight and retention times above 1e6 peak intensity were detected from the positive mode data by Compound Discoverer excluding compounds found in the blanks. Without blank removal, the number of detected MW and RT was 711. Result filters were used to filter out compounds from the table based on user defined conditions, i.e. area threshold (see Figure 4).

Unknown ID with mzCloud

Compound Discoverer 2.0 includes batch compound ID against mzCloud online HRAM fragmentation library which contains high quality curated MS/MS and Msn spectra. The search algorithm allows match with ion activation energy with user adjustable ion activation energy tolerance window (Figure 5). The sophistication in the search algorithm increases the confidence in the identifications for small molecules where fragmentation pattern changes with ion activation energies.

mzCloud hits are indicated in the Compounds table with number of hits and best match scores (Figure 6). For each hit, the spectra comparison between the query spectrum and library match spectrum is visualized in a mirrored plot (Figure 7).

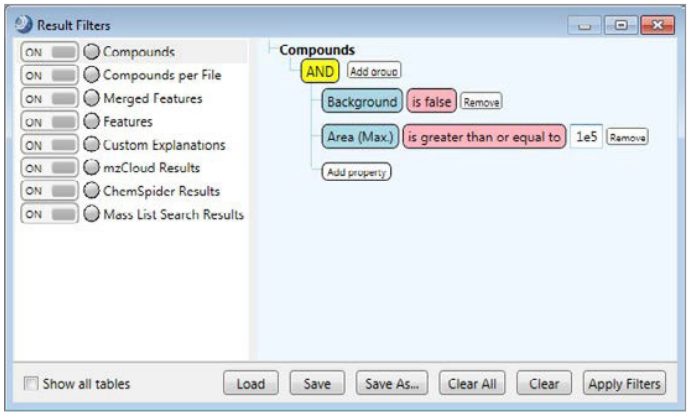

Figure 4. Result Filters.

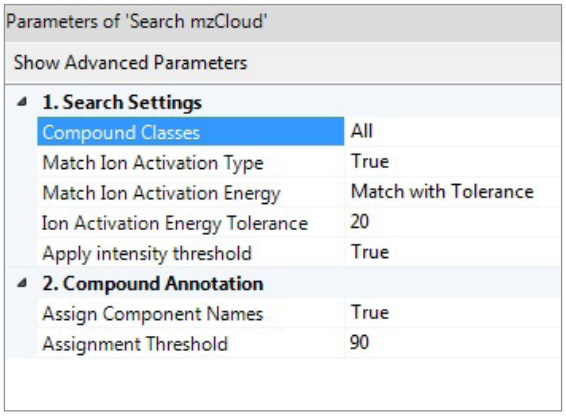

Figure 5. mzCloud node settings.

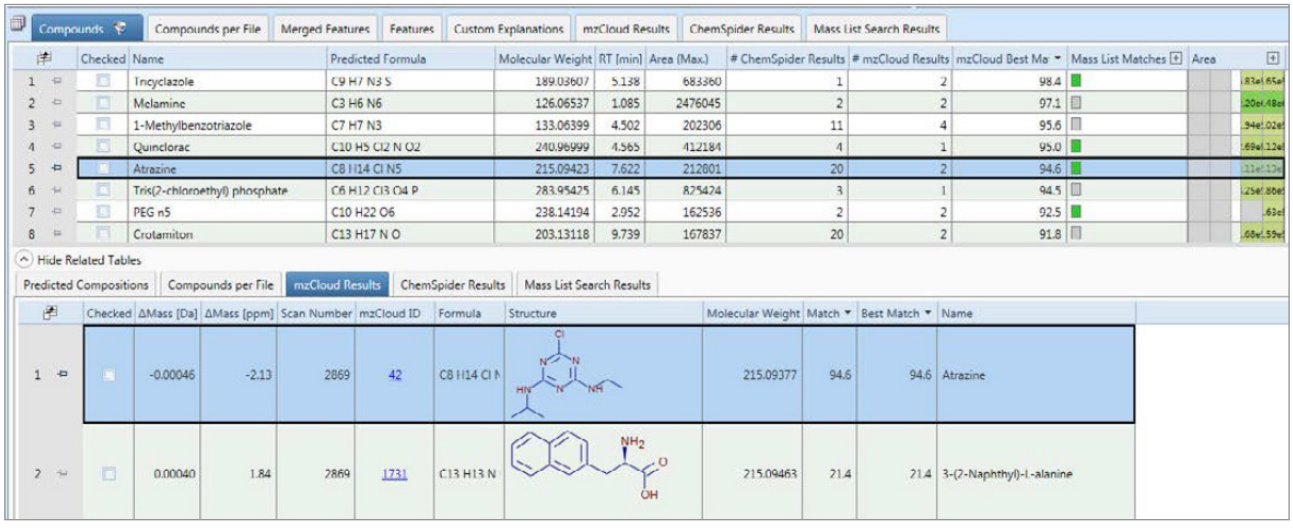

Figure 6. mzCloud hits in Compound Discoverer with match scores.

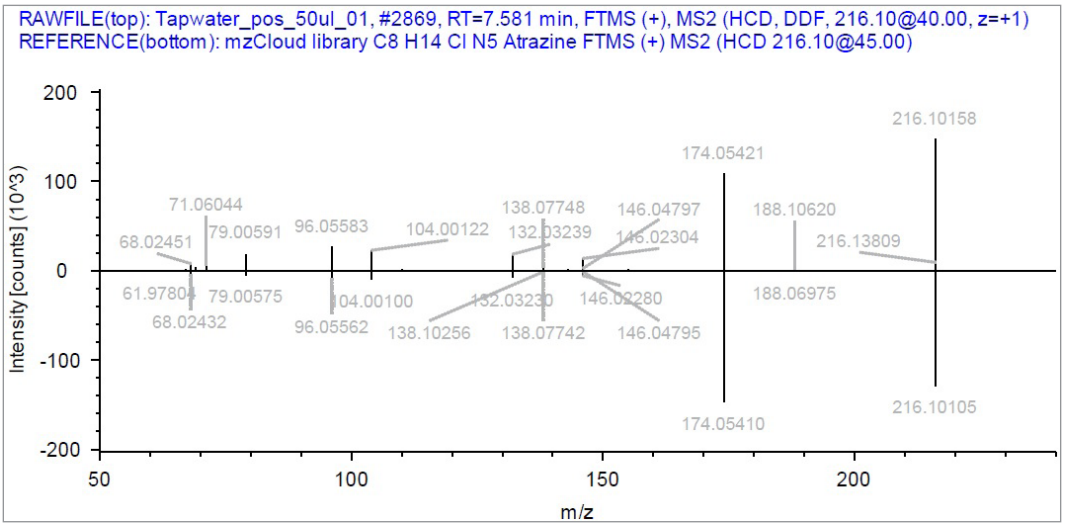

Figure 7. mzCloud hit spectral comparison between query and library spectra.

Unknown Compound Formula Prediction

Formula predictions by the Predict Composition node are listed in the sub table for each compound. The one with the best SFit% and most number of matching isotopes (#MI) is listed on the top with information like delta mass ppm. (See Figure 8)

Compounds | Compounds per File | Merged Features | Features | Custom Explanations | mzCloud Results | ChemSpider Results | Mass List Sear

	Checked	Name	Predicted Formula	Molecular Weight	RT [min]	Area (Max.)	# ChemSpider Results	# mzC
1		Tricyclazole	C9 H7 N3 S	189.03607	5.138	683360	1	
2		Melamine	C3 H6 N6	126.06537	1.085	2476045	2	
3		1-Methylbenzotriazole	C7 H7 N3	133.06399	4.502	202306	11	
4		Quinclorac	C10 H5 Cl2 N O2	240.96999	4.565	412184	4	
5		Atrazine	C8 H14 Cl N5	215.09423	7.622	212801	20	
6		Tris(2-chloroethyl) phosphate	C6 H12 Cl3 O4 P	283.95425	6.145	825424	3	
7		PEG n5	C10 H22 O6	238.14194	2.952	162536	2	
8		Crotamiton	C13 H17 N O	203.13118	9.739	167837	20	

Hide Related Tables

Predicted Compositions | Compounds per File | mzCloud Results | ChemSpider Results | Mass List Search Results

	Checked	Formula	Molecular Weight	Is known to ChemSpider	ΔMass [Da]	ΔMass [ppm]	SFit [%]	# MI	RDBE
1		C10 H5 Cl2 N O2	240.96973	X	0.00026	1.07	76	5	8.0
2		C7 H6 Cl2 F N O3	240.97088		-0.00089	-3.67	46	5	4.0
3		C5 H8 Cl2 F3 N S	240.97066		-0.00067	-2.77	46	4	0.0
4		C6 H13 Br N P S	240.96897		0.00102	4.24	0	4	1.0
5		C4 H8 Br N3 O4	240.96982		0.00017	0.72	21	3	2.0
6		C3 H5 Cl2 N7 S	240.97042		-0.00043	-1.78	17	3	4.0
7		C5 H6 Cl3 N5	240.96888		0.00111	4.62	7	3	4.0
8		C9 H5 Cl N O3 P	240.96956		0.00043	1.80	27	2	8.0
9		C7 H4 N3 O3 P S	240.97110		-0.00111	-4.59	19	2	8.0
10		C8 H5 N O4 P2	240.96938		0.00061	2.53	19	2	8.0

Figure 8. Predicted Compositions for each unknown compound listed in the sub table.

Spectral fit is visualized for each composition prediction in the spectrum window. (See Figure 9).

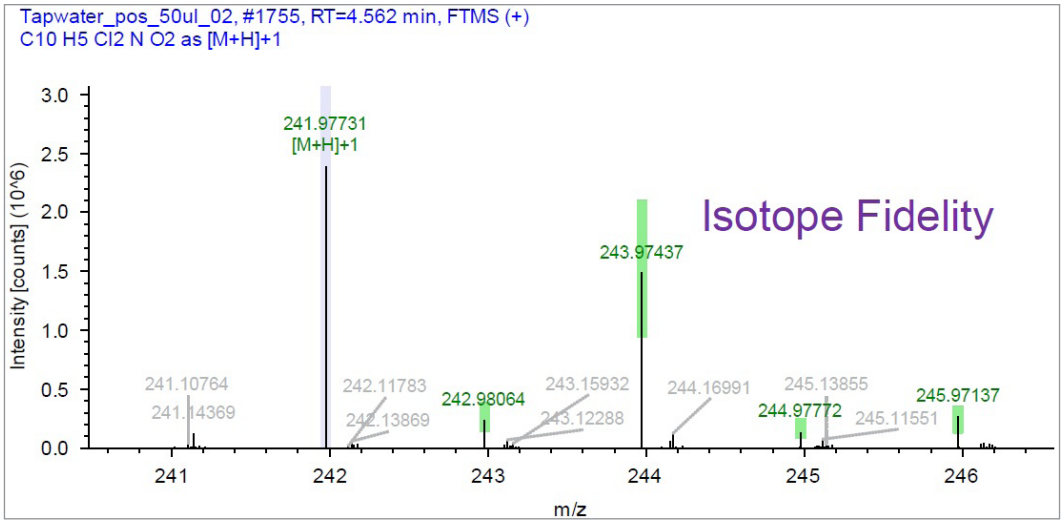

Figure 9. Spectral fit for predicted composition $C_{10}H_5Cl_2NO_2$ based on resolution.

ChemSpider Search and Custom Explanations

For the compounds that did not have match from mzCloud, ChemSpider hits were reviewed. ChemSpider search was performed using predicted formulas. If formula was not available, then accurate mass was used. The databases used were ACToR: Aggregated Computational Toxicology Resource; DrugBank; EAWAG Biocatalysis/Biodegradation Database; EPA DSSTox; FDA UNII – NLM. ChemSpider hits for each compound are listed in the sub table in the order of # of references (See Figure 10).

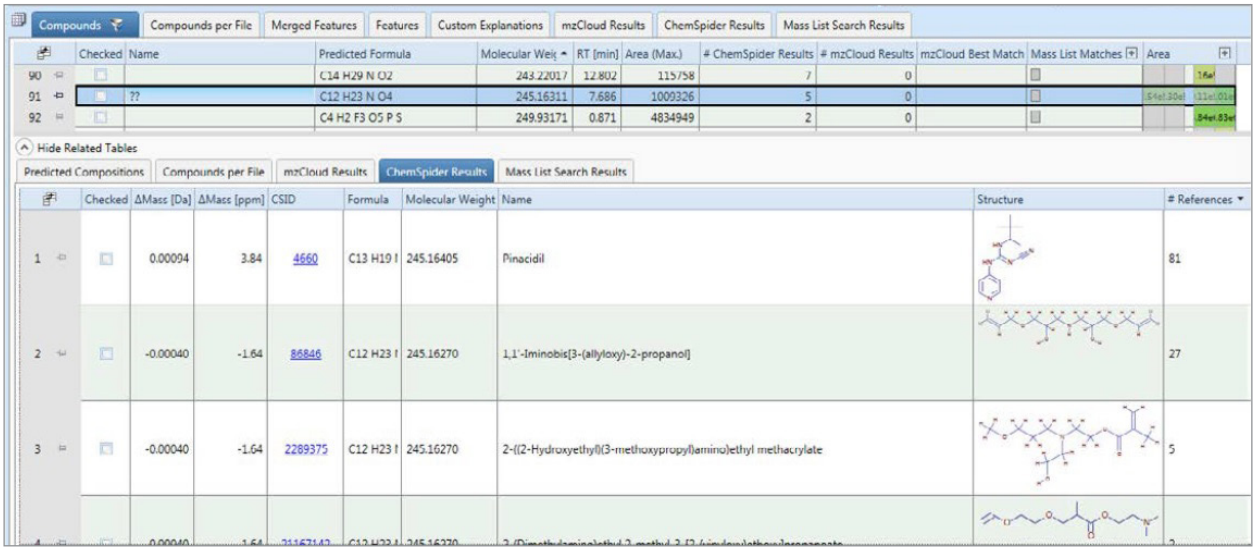

Figure 10. ChemSpider hits for each compound listed in the sub table.

The problem is how do we know if any of the ChemSpider hits is the right answer? FISh Scoring in Custom Explanations in Compound Discoverer was used to verify compound ID against MS/MS data. User proposes a structure for the compound of interest, runs FISh Scoring on the fly based on the proposed structure. FISh coverage score is calculated and fragment structures are automatically annotated. Figure 11 shows an example of FISh annotations on an unknown compound based on ChemSpider proposal.

Scan this QR code on your mzCloud app to find out what this compound is! Download the mzCloud app from your App Store on iphone or androids.

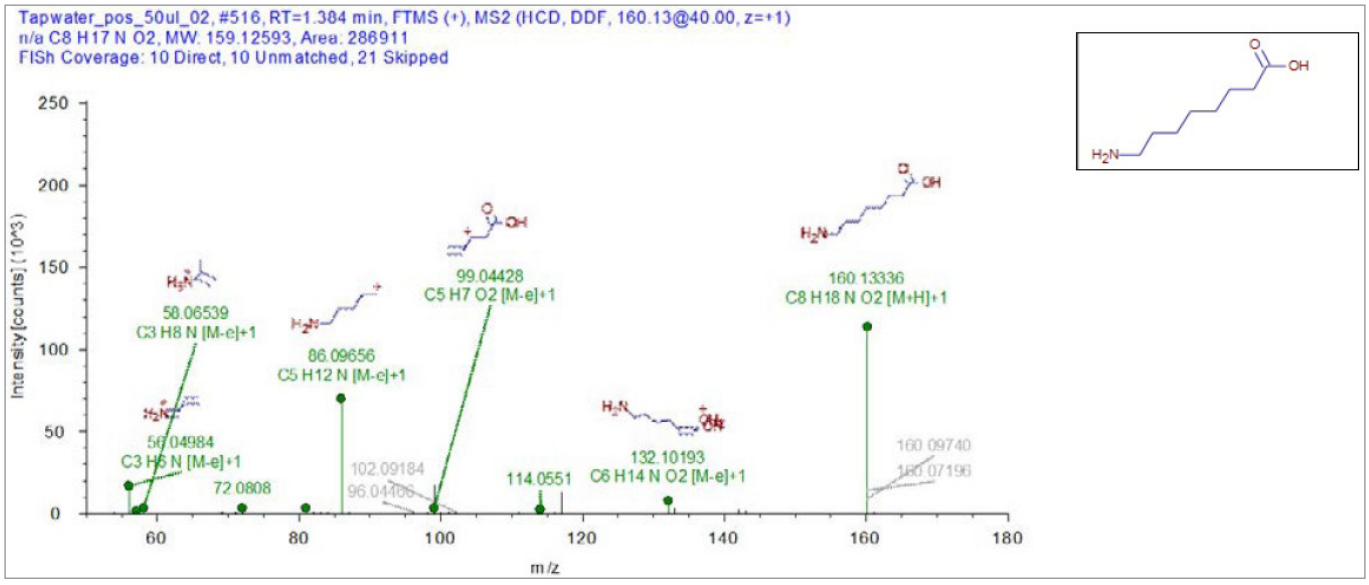

Figure 11. FISh Scoring based on proposed structure for unknown ID.

Identified Compounds

From the 185 compounds detected in the water sample, 16 of them were identified by mzCloud automatically (see Table 1). The most dominant identified compound is Melamine. Its peak intensity is about 2e7. Others include drugs, pesticides, herbicides and etc. The ones with match score > 90 are very confident identifications based on MS/MS spectrum match and collision energy match. The other unknown compounds without mzCloud hits were much more difficult to identify. A strategy of combing ChemSpider hits, delta ppm, predicted compositions, custom explanations and FISh Scoring were used to try to identify these unknowns. However, the false positive ID rate was very high.

Table 1. Unknown compounds identified by mzCloud

	Name	Formula	Molecular Weight	RT [min]	Delta ppm	Area (Max.)	ChemSpider Results	mzCloud Results	mzCloud Match Score
1	Melamine	C3H6N6	126.06537	1.09	0.17	2476045	2	2	97
2	Dextromethorphan	C18H25NO	271.19405	15.70	-1.62	2170464	8	1	85
3	hydroxycoumarin	C9H6O3	162.03184	14.53	-0.89	1456203	8	4	75
4	Tris(2-chloroethyl) phosphate	C6H12Cl3O4P	283.95425	6.15	-1.33	825424	3	1	95
5	Tricyclazole	C9H7N3S	189.03607	5.14	-0.03	683360	1	2	98
6	Quinclorac	C10H5Cl2NO2	240.96999	4.57	-1.07	412184	4	1	95
7	tri-phenylphophine oxide	C18H15OP	278.08637	9.66	-1.14	390088	2	3	72
8	Triethyl Phosphate	C6H15O4P	182.07087	4.93	-0.41	300639	4	2	90
9	8-Aminooctanoic acid	C8H17NO2	159.12606	1.47	0.83	286911	24	3	42
10	Atrazine	C8H14ClN5	215.09423	7.62	-2.13	212801	1	2	95
11	1-Methylbenzotriazole	C7H7N3	133.06399	4.50	0.06	202306	11	4	96
12	Crotamiton	C13H17NO	203.13118	9.74	-0.82	167837	20	2	92
13	PEG n5	C10H22O6	238.14194	2.95	-1.26	162536	1	2	93
14	phthalate	C12H14O4	222.08961	7.94	-1.79	162193	45	4	75
15	Indole-3-acetic acid	C10H9NO2	175.06345	3.47	-0.68	147127	24	2	67
16	Proline	C5H9NO2	115.06351	2.50	-1.53	105885	33	2	51

CONCLUSIONS

- Compound Discoverer 2.0 provides a single software solution for HRAM data processing and confident unknown compound identifications
- Unknown compound ID via batch search against mzCloud online HRAM fragmentation library proved to be the most productive and confident way for unknown compound identifications ChemSpider search combined with calculated formula from high resolution Orbitrap data complements mzCloud search but has too many false positives
- Structure elucidation using Custom Explanations and FISh Scoring in Compound Discoverer was handy and a nice way to verify ChemSpider hits against MS/MS data
- Quantitation of unknown contaminants is not the focus of this study. However, results can be exported from Compound Discoverer to software like TraceFinder for absolute quantitation.

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Quantitative Comparison of Hormones in Drinking Water Between MS/MS and Orbitrap Technology

Ali Haghani and Andy Eaton, *Eurofins Eaton Analytical, Inc. Monrovia, CA*
Richard F. Jack, Claudia P. B. Martins, and Dipankar Ghosh, *Thermo Fisher Scientific, San Jose, CA*

GOAL

To demonstrate a liquid chromatography high-resolution, accurate mass (LC-HRAM) methodology using Orbitrap technology as a sensitive, accurate, and reliable alternative to the use of triple quadrupoles mass spectrometers in the quantification of hormones in drinking water according to EPA guidelines.

Keywords: Contaminants of emerging concern, CEC, endocrine disrupting compound, EDC, micropollutants, EPA Method 539, Q Exactive

INTRODUCTION

Increasingly, contaminants of emerging concern (CEC) including pharmaceuticals and personal care products, such as the contraceptive pill and antibiotics, are being detected at low levels in surface water. Many of these CEC are endocrine disrupting compounds (EDCs), which can alter the normal functions of hormones and cause a variety of health effects [1,2]. As a result, the United States Environmental Protection Agency (EPA) has developed EPA Method 539 [3] for the Unregulated Contaminant Monitoring Rule 3 (UCMR 3) program, which collects data for contaminants suspected to be present in drinking water but that do not have health-based standards set under the Safe Drinking Water Act (SDWA) [4].

The identification and quantification of micropollutants at low concentrations requires both sensitivity and selectivity against complex matrices. Selected reaction monitoring (SRM) of precursor-product ion transitions, which makes use of a triple quadrupole mass analyzer, has been the method of choice [5]. However, other screening strategies employing full scan mode and other advanced MS/MS scan modes can potentially offer a valuable alternative to SRM based methodology due to the development of more rugged, sensitive, and selective instrumentation.

The quantitative performance of the latest generation of high-resolution instruments is comparable to that of a triple quadrupole MS, even though different scanning modes are used. Higher-resolution instrumentation also allows flexibility concerning compound identification because the experiment can be set up for targeted quantitation, screening, or both. In an Orbitrap-based instrument, the parallel reaction monitoring (PRM) mode performs most closely to a triple quadrupole mass analyzer using SRM mode. This study compares the quantitation performance between a triple quadrupole (MS/MS) to that of an Orbitrap-based detector using EPA Method 539: *Determination of Hormones in Drinking Water by Solid Phase Extraction (SPE) and Liquid Chromatography Electrospray Ionization and Tandem Mass Spectrometry (LC-ESI-MS/MS).* All other aspects of the method including sample preservation, storage, preparation, and chromatographic separation were kept the same. The only difference was the MS detector.

EXPERIMENTAL

Sample Preparation

The sample preparation is based on EPA Method 539. Any modifications and text are highlighted for clarity and discussion purposes. Five hundred milliliters of a dechlorinated sample with Omadine™ biocide

was extracted through solid phase extraction (SPE) using an octadecyl (C-18) stationary phase after adding surrogates. The eluent from SPE was concentrated to dryness and then diluted to 1 mL with 50:50 methanol/water. An aliquot was injected into the LC-MS/MS after adding internal standards and quantified against the internal standard (IS).

LC-MS Conditions

Under the EPA Method, flexibility is allowed for columns, eluents, and MS conditions in general. Table 1 shows the conditions optimized and used in the analysis.

Table 1. LC-MS conditions optimized and used for the experiments described

Mass Analyzer	**Thermo Scientific™ Q Exactive™ Hybrid Quadrupole-Orbitrap™ Mass Spectrometer**
Mass Resolving Power	70,000 (FWHM) at *m/z* 200
Scan Mode	PRM
AGC	2e5
IT	200 ms
Isolation Window	1.0 *(m/z)*
HPLC	Thermo Scientific™ UltiMate™ 3000 RS UHPLC, binary pump, autosampler, and column heater with 100 µL sample loop
Column	Thermo Scientific™ Acclaim™ PolarAdvantage II (2.1 x 150 mm, 3 µm, 120 Å, P/N 063187)
Eluents	A) 1 mM ammonium fluoride in water; B) 50:50 (v/v) acetonitrile/methanol; Gradient flow at 0.3 mL/min with a 21.4 min run
Injection Volume	50 µL

EPA Method 539 uses a triple quadruple method using an SRM scan mode (also known as MRM). According to EPA Method 539, section 3.16, "MRM... a mass spectrometric technique in which a precursor ion is first isolated, then subsequently fragmented into a product ion(s). Quantitation is accomplished by monitoring a specific production". In this study, a similar set of conditions was used.

In PRM mode, a list of targeted precursor ions, retention times, and collision energies can be included in the method. When detecting a targeted ion, the system isolates that precursor ion in the quadrupole and triggers MS/MS experiments, generating MS/MS spectra that can be used for both quantitation and identification. Both the quantitation and identification are performed taking into account product ions generated after the isolation of a specific precursor ion. This operating mode is similar to an SRM (or MRM) experiment using a triple quadrupole instrument. In PRM mode, the third quadrupole is substituted with an HRAM (high-resolution, accurate mass) mass analyzer, enabling the parallel detection of all target product ions (Figure 1).

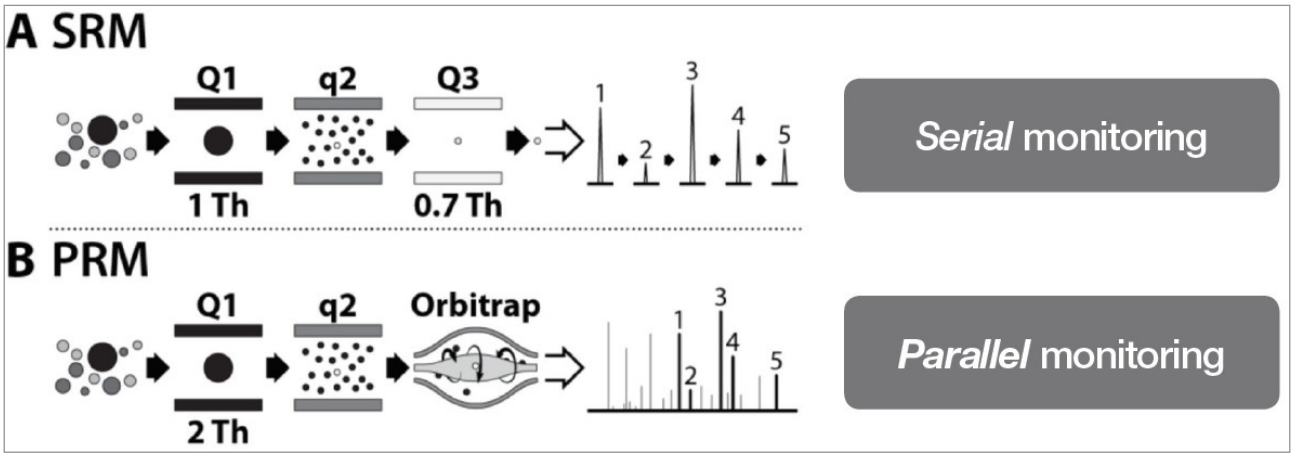

Figure 1. Schematic representation of selective reaction monitoring (SRM) mode and parallel reaction monitoring (PRM) mode.

The number of scans across the chromatographic peak is dependent on the cycle time of the instrument and, therefore, on the set of conditions used (e.g., resolving power). These conditions can and should be optimized depending on the objectives of the experiment. In this case, accurate quantitation as well as unambiguous identification has been targeted. Optimized conditions can be found in Table 1.

Requirements

The EPA has strict requirements that should be met before the analysis of any sample, referred to as the Initial Demonstration of Capability (IDC). These requirements include the demonstration of low background noise, precision by analyzing four to seven extracted laboratory fortified reagent water blanks (LFB) at mid-level, the demonstration of accuracy and, finally, the demonstration of capability necessary to meet the minimum reporting limit (MRL). The percent relative standard deviation (%RSD) of the results of the replicate analyses must be ≤ 20%. The average percent recovery for each analyte must be within ± 30% of the true value.

RESULTS AND DISCUSSION

Excellent linearity has been demonstrated from a range starting at one-fourth of the MRL (Figure 2). Table 2 compares the MRL and LCMRL obtained when using both SRM and PRM modes. Tables 3, 4, and 5 summarize precision and accuracy of the method after the LC-HRAM analysis of different types of samples – reagent water spiked at different levels and UCMR3 water samples.

As shown in Table 2, the LCMRL and DL were much lower when using LC-HRAM than the detection limits reported in EPA Method 539. This demonstrates the greater sensitivity using Orbitrap HRAM compared to the MS/MS and hybrid instruments used during method validation. In order to demonstrate method robustness, the EPA requires the demonstration of performance using a fortified matrix in blanks, reagent water, and real samples. Results are summarized in Tables 3, 4, and 5.

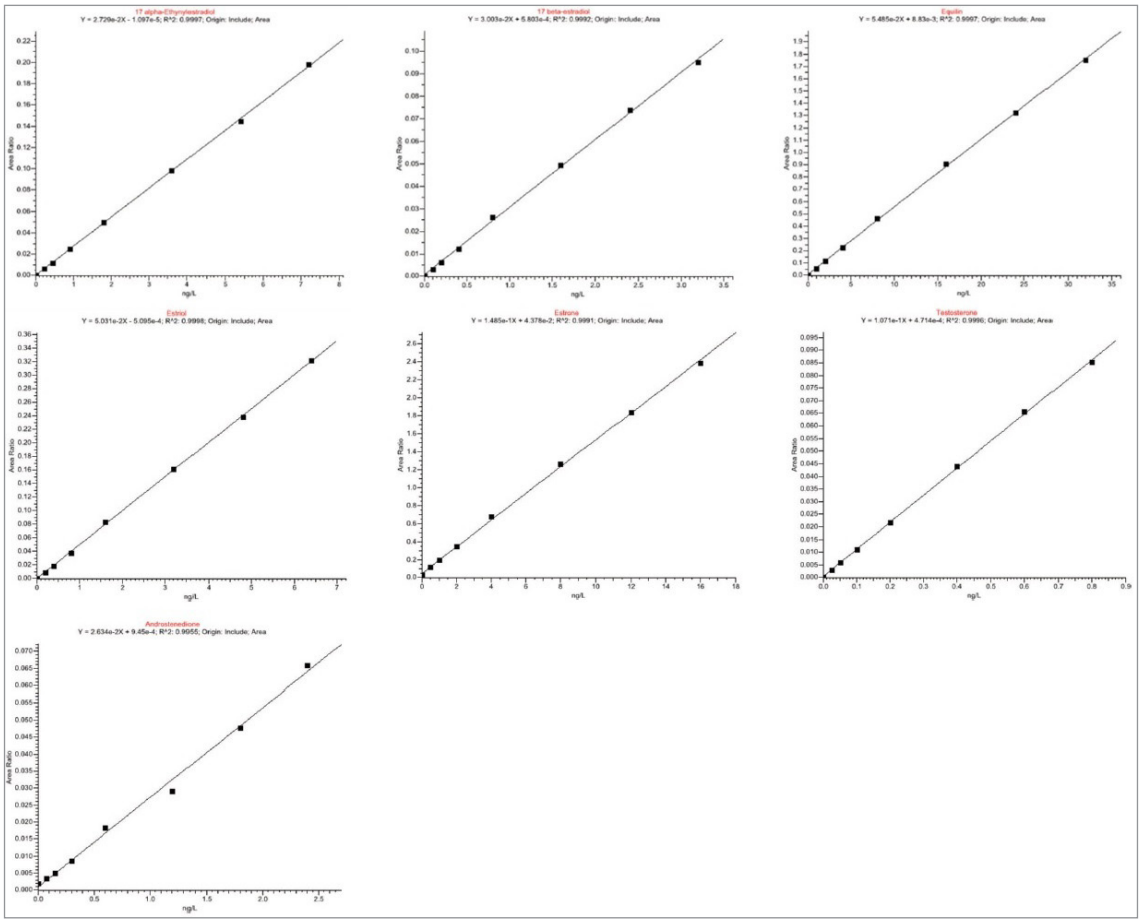

Figure 2. Calibration curves for all EPA Method 539 analytes.

Table 2. MRL and LCMRL comparison when using triple quadrupole and Orbitrap mass analyzers in reagent water preserved according to EPA Method 539

Analyte	UCMR3 MRL (ng/L)	EPA 539 published LCMRL (ng/L)	LC-HRAM[a] LCMRL (ng/L)	LC-HRAM[a] LCMRL Calc -DL (ng/L)
17α-ethynylestradiol	0.9	1.3	Critical level 0.05[b]	0.1
17β-estradiol	0.4	0.32	0.17	0.047
equilin	4	0.28	Critical level 0.23[b]	0.48
estriol	0.8	3	0.27	0.2
estrone	2	4	0.84	0.48
testosterone	0.1	0.062	0.033	0.027
4-androstene-3,17-dione	0.3	0.37	0.19	0.08

[a]The detection limits reported in EPA Methos 539 reflect the MS/MS, Ion Trap, and Hybrid MS technology used at the time of method validation. They are shown here for reference purposes. Detection limits for newer MS/MS instruments can either be lower or higher depending on many variables including operator performance, instrumentation, sample preparation, and other factors. Thus, the lower DL for Orbitrap technology shown here demonstrate that quantitatively the results are comparable with the reported method.

[b]The critical level calculation can't find the MRL as the lowest standard wasn't low enough for exact determination. Thus, a lower level spiking concentration is required to determine the LCMRL for these compounds.

Table 3. LC-HRAM method: Precision and accuracy in fortified reagent water spiked at 10 x MRL

Analyte	Fortified Concentration (ng/L)	Avg. Recovery (%)	RSD (%)
17α-ethynylestradiol	7.2	82	4
17β-estradiol	3.2	84	3
equilin	32.0	81	3
estriol	6.4	100	4
estrone	16.0	83	4
testosterone	0.8	87	5
4-androstene-3,17-dione	2.4	85	8

n=4

Table 4. LC-HRAM method: Precision and accuracy in fortified matrix (UCMR3 water sample 1) spiked at MRL

Analyte	Fortified Concentration (ng/L)	Avg. Recovery (%)	RSD (%)
17α-ethynylestradiol	0.72	95	2
17β-estradiol	0.32	87	1
equilin	3.20	92	8
estriol	0.64	101	4
estrone	1.60	95	3
testosterone	0.08	99	0.1
4-androstene-3,17-dione	0.24	118	0.1

n=4

Table 5. LC-HRAM method: Precision and accuracy in fortified matrix (UCMR3 water sample 2) spiked at 10 × MRL

Analyte	Fortified Concentration (ng/L)	Avg. Recovery (%)	RSD (%)
17α-ethynylestradiol	7.2	98	3
17β-estradiol	3.2	113	0.8
equilin	32.0	102	0.7
estriol	6.4	103	2.4
estrone	16.0	110	1.7
testosterone	0.8	103	0.3
4-androstene-3,17-dione	2.4	104	1.4

n=4

CONCLUSION

The LC-HRAM methodology proved to be sensitive, accurate, reproducible, and a reliable alternative to the use of triple quadrupoles in the quantification of hormones in drinking water according to the EPA guidelines. By the use of different scanning modes within the Q Exactive MS, quantitation on precursor ions and identification of fragments ions are possible. These scanning modes are consistent with the requirements in many regulated methods and can possibly be used for compliance monitoring in place of a triple quadrupole MS. The latest LC-HRAM technology assures sensitivity and selectivity in the quantitation of known contaminants in drinking water, while potentially enabling the combination of targeted and non-targeted analysis in the same run, which cannot be accomplished using MS/MS alone.

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Rare Earth Element Determination in Heavy Crude Oil by USN-ICP-MS After Digestion Using Single Reaction Chamber (SCR) Technology

Gabriel T. Druzian, Leticia S. F. Pereira, Paola A. Mello, Marcia F. Mesko, Fabio A. Duarte and Erico M. M. Flores

INTRODUCTION

Elemental analysis of heavy crude oil is important for a variety of reasons including region of origin, maturity, migration, type, and identification of potential challenges that could arise during the refining process. There are numerous challenges with analysis of heavy crude oil with most being centered on the sample prep process due to the complexity of the sample matrix. Microwave digestion has been used to overcome some of these challenges, however, traditional rotor based systems still face problems with limits of quantification due to sample size limitations, temperature and pressure capabilities, high residual organic contact (ROC), and high residual acidity. The revolutionary Milestone's Single Reaction Chamber (SRC) microwave digestion incorporates all of the benefits of closed vessel microwave digestion while making sample preparation fast, easy, effective, and the highest quality. SRC operates at very high temperature and pressure (300 °C and 199 bar respectively), thus complete digestion of even the largest sample size and most reactive samples can be achieved. The sample can be weighed directly into a disposable glass vial, eliminating the need for acid cleaning and vessel assembly. The paper "*Rare earth element determination in heavy crude oil by USN-ICP-MS after digestion using a microwave-assisted single reaction chamber*", Druzian et al, *J. Anal. At. Spectrom*., 2016, 31, 1185, provide evidence of the digestion quality obtained with Milestone's ultraWAVE in comparison with a rotor based echnology.

ABSTRACT

In this work a method for rare earth element (REE) determination by inductively coupled plasma mass spectrometry (ICP-MS) with an ultrasonic nebulizer (USN) was proposed after heavy crude oil digestion by microwave-assisted wet digestion (MAWD) using a single reaction chamber (SRC) system. Operational conditions of the MAWD-SRC method, such as sample mass (from 250 to 1000 mg), type and volume of digestion solutions, temperature achieved during digestion (from 200 to 270 ºC) and microwave irradiation time (35, 40, 45 and 50 min) were investigated.

Using optimized digestion conditions, the carbon concentration and residual acidity in digests were 2345 mg L^{-1} and 14.6%, respectively.

Since the acidity was low and dilution was not required after digestion by the MAWD-SRC method, lower limits of quantification (LOQs) were obtained (0.1 up to 2 ng g^{-1}) and the determination of some analytes present in very low concentration was possible. It was possible to digest a relatively high crude oil mass (up to 1 g) using 8 mL of 14.4 mol L^{-1} HNO_3 in just 40 min, which can be considered as an important aspect taking into account the difficulties involved in heavy crude oil digestion for further REE determination by ICP-MS. The accuracy was evaluated by analyte spike and also by comparison of results obtained by MAWD-SRC with those using conventional MAWD and also by microwave-induced combustion. Suitable recoveries were obtained for all analytes (94 to 110%) and no statistical difference was observed between the results obtained by MAWD-SRC and those using other methods.

INSTRUMENTATION

Figure 1. Milestone's ultraWAVE

An ultraWAVE digestion system, based on a single reaction chamber (SRC) equipped with five quartz vessels (total volume of 40 mL) was used for crude oil digestion (MAWD-SRC method). The SRC features a large 1 Liter pressurized stainless steel reaction chamber, which also serves as the microwave cavity.

Samples are weighed into auto sampler-type vials with the appropriate digestion acid and loaded into a rack. The rack is loaded into the chamber, which is then sealed and pre-pressurized with nitrogen to 40 bar prior to microwave heating. Pre-pressurization prevents splashing or boiling of the sample solutions, which prevents cross contamination or loss of volatiles. Because the pressure in the chamber increases with sample temperature, boiling never occurs.

SRC can operate at very high temperature and pressure – up to 300 ºC and 199 bar, which enables the complete digestion of every sample-type. The higher pressure capability of a SRC allows higher sample weights to be digested. With SRC, different sample types can be run simultaneously – there is no need to "batch" digestion runs into identical sample types as with traditional microwave digestion. The SRC also requires less digestion acid, which lowers the reagent blank and the ultra-pure reagent costs.

On completion of the program, the chamber automatically vents and the rack is removed. Samples are diluted to volume in the vials, ready for aliquoting and measurement.

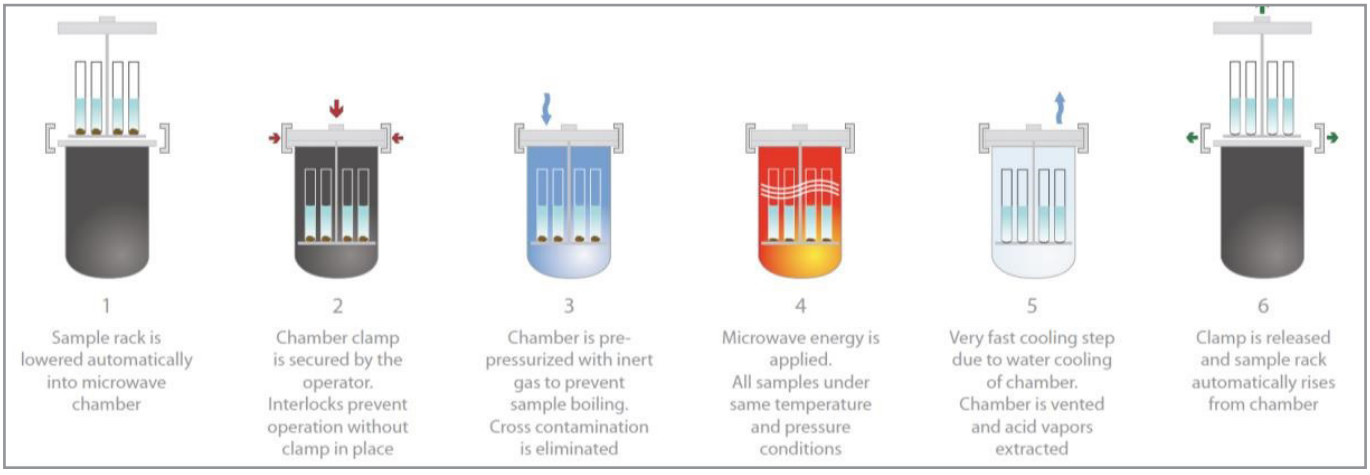

Figure 2. – Workflow of the ultraWAVE

RESULTS AND CONCLUSIONS

To the best of the authors' knowledge, this is the first method able to digest 1 g of crude oil using wet digestion in closed vessels. This fact allowed the determination of those elements present at very low concentration in crude oil. This article is another clear evidence on the reliability of SRC technology.

The ultraWAVE ensures complete digestion of all sample sizes, while the rotor-based technology shown a much higher carbon concentration due to the low digestion temperatures attained. Digestion efficiency using the ultraWAVE was higher, providing low residual carbon and acidity in digests, which are important parameters to avoid interferences during the determination of REE by ICP-MS.

The ultraWAVE combined good performance, safety and relatively high sample throughput since the digestion could be performed in multiple positions in as little as 40 minutes.

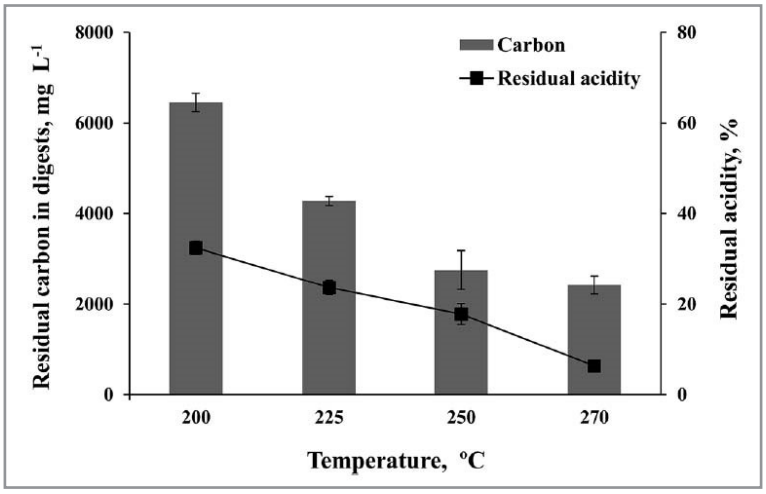

Figure 3. Effect of temperature in the digestion of crude oil "A" by MAWD-SRC (mean and standard deviation, n=3). Digestion was performed using 750 mg, 6 mL of 14.4 mol L^{-1} HNO_3 as the digestion solution and a microwave irradiation time of 40 min.

Finally, LOQs (limit of quantitation) were lower than those obtained using the conventional microwave system, as well as residual acidity.

REFERENCES

Abstract, graph and main part of the text of this report is taken from: "Rare earth element determination in heavy crude oil by USN-ICP-MS after digestion using a microwave-assisted single reaction chamber" Druzian et al, *J. Anal. At. Spectrom*., 2016, *31*, 1185 (https://doi.org/10.1039/C6JA00050A).

FURTHER READINGS

To learn more about ultraWAVE and other related topics, feel free to visit these websites:
Milestone ultraWAVE – SRC Technology: https://www.milestonesrl.com/products/microwave-digestion/ultrawave
Milestone srl: http://www.milestonesrl.com

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Orbitrap is an ion trap mass analyzer that consists of two outer electrodes and a central electrode, which enable it to act as both an analyzer and detector. Ions entering the Orbitrap are captured through "electrodynamic squeezing," after which they oscillate around the central electrode and in between the two outer electrodes. Different ions oscillate at different frequencies, resulting in their separation. By measuring the oscillation frequencies induced by ions on the outer electrodes, the mass spectra of the ions are acquired using image current detection.

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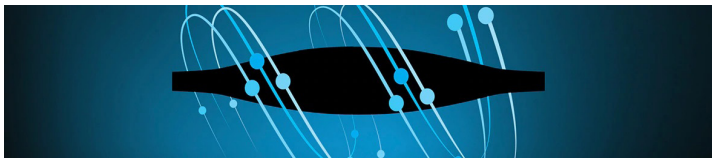

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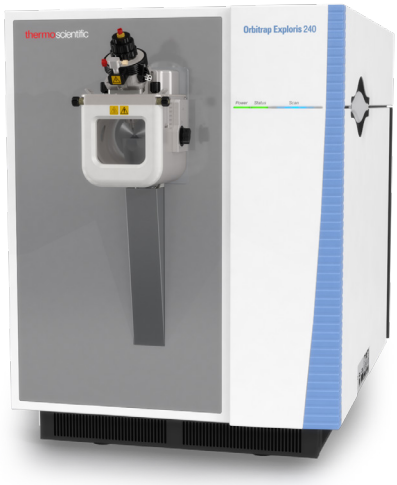

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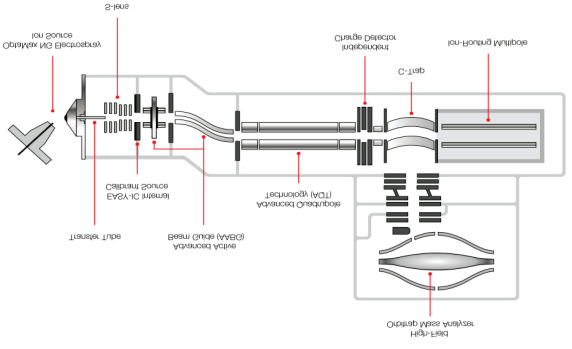

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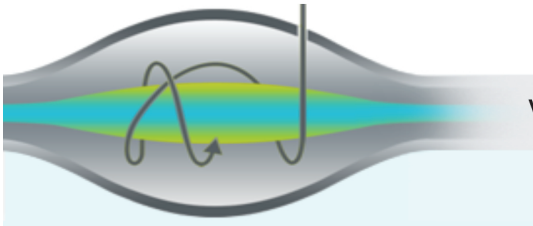

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Milestone ultraWAVE is the Benchmark in Microwave Digestion

The Milestone ultraWAVE isn't just an evolution; it's a revolution - changing how industrial and research laboratories around the world prep samples for analysis. Milestone patented ultraWAVE Single Reaction Chamber (SRC) technology transcends traditional closed and open vessel digestion, offering significantly greater digestion capabilities for even the most difficult sample types.

High-performance stainless-steel construction allows for higher pressures and temperatures, while disposable vessels eliminate the need to assemble, disassemble or clean between processing. Just as important, dissimilar samples can be processed simultaneously, saving time and money.

Enhanced Efficiency in Sample Preparation for Metals Analysis

The SRC technology achieves extraordinary performance capabilities combining microwave heating with a high-pressure reactor which acts simultaneously as microwave cavity and vessel.

The ultraWAVE is easy to use, cost-effective, quick to adopt, and fast to implement. The ultraWAVE has already transformed and enhanced the way analytical chemists prepare their samples for trace metal analysis in hundreds of laboratories all over the world. The ultraWAVE represents the state-of- the-art in microwave sample preparation, overcoming the limitations of the conventional digestion systems.

One Method for All Samples

Any combination of sample types (food, environmental, polymer, cosmetic, pharmaceutical, geological, chemical, and petrochemical) can be digested simultaneously. No method development is needed, as the same method can be used for nearly any sample. For the first time, blanks and reference standards of any matrix can be digested alongside samples. The ultraWAVE dramatically improves the lab workflow, as it allows to run any matrices simultaneously in a single digestion cycle.

Unrivalled Performance for Superior Digestion Quality

Operating up to 199 bar and 300 °C, the ultraWAVE enables the complete digestion of extremely difficult samples and large amounts of organics. Unlike conventional microwave digestion systems, every sample is under direct temperature and pressure control, so there is no need to rely on a reference vessel or indirect control such as infrared temperature sensors. The ultraWAVE reaches high temperatures faster, cools faster (10 min from 200°C to room temperature), and is capable of higher pressure and temperature than any other system, expanding the digestion efficiency. The ultraWAVE does not suffer any cross contamination between samples. Blanks are significantly lower than with conventional microwaves since less acid is used, and vials have a much less surface in contact with the analytical solution.

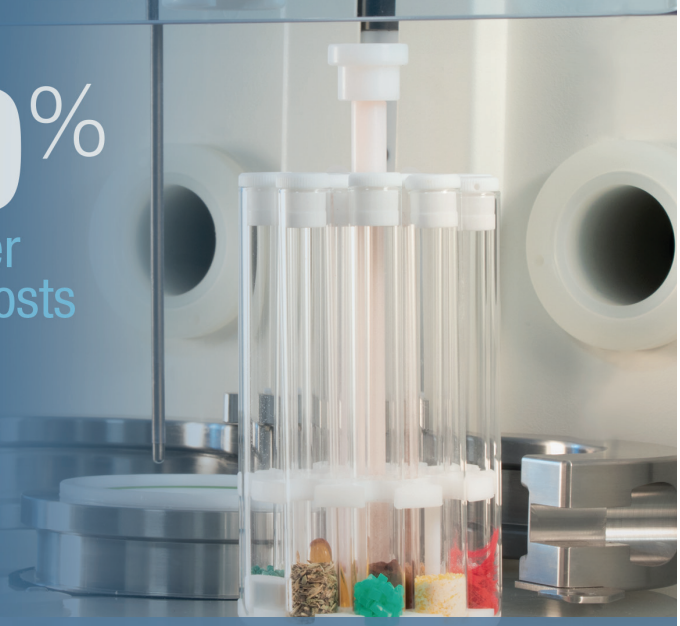
Green Digestion

The ultraWAVE allows for the complete digestion of organic samples with diluted nitric acid only with clear benefits for the subsequent analytical step and for the environment.

High Productivity

High sample throughput and quick turnaround time are top priorities in most analytical laboratories, along with high quality of the analysis and low running costs. The Milestone ultraWAVE fully matches these requirements.

50% reduction in cycle time | **2X** the throughput | **50%** lower labor costs



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Webinar

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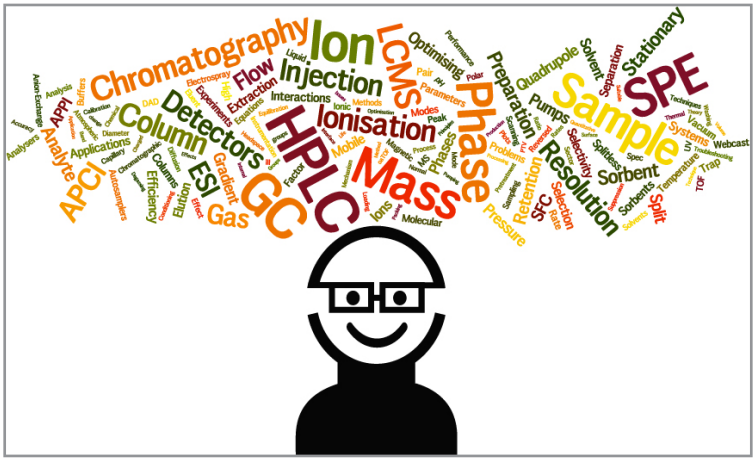

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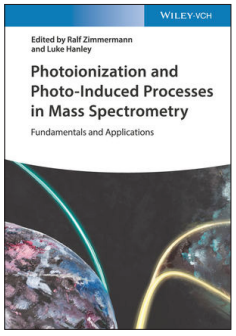
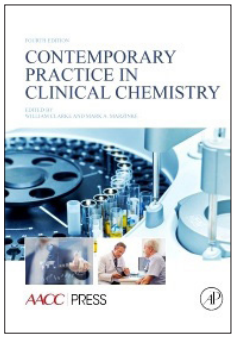
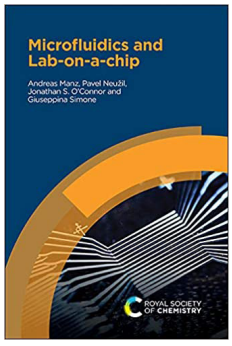


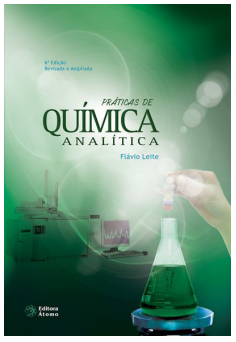
Photoionization and Photo-Induced Processes in Mass Spectrometry: Fundamentals and Applications
Ralf Zimmermann, Luke Hanley (Editors)
September 2020. Publisher: John Wiley & Sons
This book provides comprehensive coverage of laser-induced ionization processes for mass spectrometry analysis. This reference for analytical scientists covers both the theory and current applications of photo-induced ionization processes. It places widely used techniques such as MALDI side by side with more specialist approaches such as REMPI and RIMS, and discusses leading edge developments in ultrashort laser pulse desorption. Read more …



Contemporary Practice in Clinical Chemistry – 4th Edition
William Clarke, Mark Marzinke (Editors)
June 2020. Publisher: Elsevier
This new edition is useful for students, residents and fellows in clinical chemistry and pathology, presenting an introduction and overview of the field to assist readers as they in review and prepare for board certification examinations. For new medical technologists, the book provides context for understanding the clinical utility of tests that they perform or use in other areas in the clinical laboratory. For experienced laboratorians, this revision continues to provide an opportunity for exposure to more recent trends and developments in clinical chemistry. Read more …



Microfluidics and Lab-on-a-chip
Jonathan S. O'Connor, Andreas Manz, Pavel Neužil, Giuseppina Simone (Authors)
August, 2020. Publisher: Royal Society of Chemistry
Covering the fast and dynamic development of miniaturization, μTAS and microfluidics, this book provides the tools for analysing phenomena from the scientific point of view and aids for implementing quan/qual models including applications in cell biology and bioanalytical chemistry. Providing a short, affordable text for a wide audience, students that for the first time approach the field, as well as engineers, physicians, cell biologists, biochemists, microbiologists, geneticists, and medical researchers. Read more …



***Práticas de Química Analítica* – 6th Edition**
Flávio Leite, Author
2020. Publisher: Editora Átomo
This book is a set of experiments that range from the simplicity of a volumetric analysis to a more elaborate study, involving wet techniques and instrumental analyzes. The procedures use samples of real life and aim to get closer to professional work by promoting technical discussions between students and professors. With proper guidance, professors will be able to carry out these experimental activities for different university degrees, as well as for students in technical high schools. Read more …

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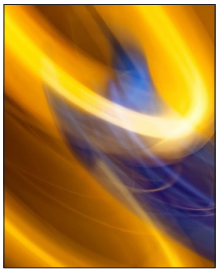

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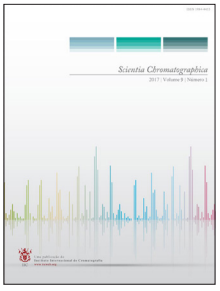

Scientia Chromatographica

Scientia Chromatographica is the first and to date the only Latin American scientific journal dedicated exclusively to Chromatographic and Related Techniques (Mass Spectrometry, Sample Preparation, Electrophoresis, etc.). With a highly qualified and internationally recognized Editorial Board, it covers all chromatography topics (HPLC, GC, SFC) in all their formats, in addition to discussing related topics such as “The Pillars of Chromatography”, Quality Management, Troubleshooting, Hyphenation (GC-MS, LC-MS, SPE-LC-MS/MS) and others. It also provides columns containing general information, such as: calendar, meeting report, bookstore, etc. Read more

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EVENTS 2020

It is suggested to consult the event's official website for updates.

August 31 – September 4
Belgrade Online — previously 71st Annual Meeting of the International Society of Electrochemistry — "Electrochemistry towards Excellence"
https://annual71.ise-online.org/

Octorber 5 – 16
VIRTUAL 43rd Annual Meeting of the Brazilian Chemical Society (43rd RASBQ)
http://www.sbq.org.br/43ra/

October 7 – 9
FCE Pharma, International Exhibition of Technology for the Pharmaceutical Industry
São Paulo Expo, São Paulo, SP, Brazil
https://www.fcepharma.com.br/

October 20 – 21
18th Congress on Quality in Metrology (ENQUALAB 2020)
São Paulo, SP
https://www.enqualab.net/

November 8 – 11
National Meeting on Forensic Chemistry (7th EnqFor) & 4th Meeting of the Brazilian Society of Forensic Sciences (SBCF)
Ribeirão Preto, SP, Brazil
https://www.en.enqfor2020.sbcf.org.br/

December 10 – 11
International Conference on Metrology, Measurement and Inspection (ICMMI 2020)
New York City, USA
https://waset.org/metrology-measurement-and-inspection-conference-in-december-2020-in-new-york

EVENTS 2021

February 07 – 11
XXIII International Mass Spectrometry Conference (IMSC 2021)
Windsor Oceânico Hotel, Rio de Janeiro, RJ, Brazil
https://www.imsc2020.com/

October 11 – 15
34th Latin American Congress of Chemistry – CLAQ 2020; 18th Latin American Congress of Chromatography – COLACRO; 10th Colombian Congress of Chromatography – COCOCRO; 4th Colombian Congress of Biochemistry and Molecular Biology - C2B2
Convention Center, Cartagena de Indias, Colombia
https://claq2020.com/en/bienvenida/

GUIDELINES FOR AUTHORS

Scope

The *Brazilian Journal of Analytical Chemistry* (BrJAC) is dedicated to the diffusion of significant and original knowledge in all branches of Analytical Chemistry. BrJAC is addressed to professionals involved in science, technology and innovation projects in Analytical Chemistry, at universities, research centers and in industry.

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BrJAC is a quarterly journal that, in addition to scientific articles and technical notes, also publishes reviews, interviews, points of view, letters, sponsor reports, and features related to analytical chemistry.

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- **Articles:** Full descriptions of an original research finding in Analytical Chemistry. Articles undergo double-blind full peer review.
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- **Technical Notes:** Concise descriptions of a development in analytical method, new technique, procedure or equipment falling within the scope of BrJAC. Technical notes also undergo double-blind full peer review.
- **Letters:** Discussions, comments, suggestions on issues related to Analytical Chemistry, and consultations to authors. Letters are welcome and will be published at the discretion of the BrJAC editor-in-chief.

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The mandatory files to be uploaded are: **Cover letter**, **Manuscript** and **Title Page** (double-blind review). **Templates** for these files are available at http://brjac.com.br/guidelines-download.php

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Examples of reference formatting

Journals

1. Orlando, R. M.; Nascentes, C. C.; Botelho, B. G.; Moreira, J. S.; Costa, K. A.; Boratto, V. H. M. *Anal. Chem*., **2019**, *91* (10), pp 6471-6478 (https://doi.org/10.1021/acs.analchem.8b04943).
   - *Publications with more than 10 authors, list the first 10 authors followed by a semicolon and et al.*
   - *Titles of journals must be abbreviated as defined by the Chemical Abstracts Service Source Index (http://cassi.cas.org/search.jsp).*

Electronic journals

2. Sapozhnikova, Y.; Hoh, E. *LCGC North Am*., **2019**, *37* (1), pp 52-65. Available from: http://www.chromatographyonline.com/suspect-screening-chemicals-food-packaging-plastic-film-comprehensive-two-dimensional-gas-chromatogr [Accessed 20 January 2019].

Books

3. Burgot, J.-L. *Ionic Equilibria in Analytical Chemistry*. Springer Science & Business Media, New York, **2012**, Chapter 11, p 181.
4. Griffiths, W. J.; Ogundare, M.; Meljon, A.; Wang, Y. Mass Spectrometry for Steroid Analysis. In: Mike, S. L. (Ed.). *Mass Spectrometry Handbook*, v. 7 of Wiley Series on Pharmaceutical Science and Biotechnology: Practices, Applications and Methods. John Wiley & Sons, Hoboken, N.J., **2012**, pp 297-338.

Standard methods

5. International Organization for Standardization. ISO 26603. Plastics — *Aromatic isocyanates for use in the production of polyurethanes — Determination of total chlorine*. Geneva, CH: ISO, **2017**.

Master's and doctoral theses or other academic literature

6. Dantas, W. F. C. *Application of multivariate curve resolution methods and optical spectroscopy in forensic and photochemical analysis*. Doctoral thesis, **2019**, Institute of Chemistry, University of Campinas, Campinas, SP, Brazil.

Patents

7. Trygve, R.; Perelman, G. US 9053915 B2, June 9, **2015**, Agilent Technologies Inc., Santa Clara, CA, US.

Web pages

8. http://www.chromedia.org/chromedia [Accessed 10 January 2019].

Unpublished source

9. Viner, R.; Horn, D. M.; Damoc, E.; Konijnenberg, A. *Integrative Structural Proteomics Analysis of the 20S Proteasome Complex* (WP-25). Poster presented at the XXII International Mass Spectrometry Conference (IMSC 2018) / August 26-31, **2018**, Florence, IT.
10. Author, A. A. *J. Braz. Chem. Soc*., in press.
11. Author, B. B., **2019**, submitted for publication.
12. Author, C. C., **2019**, unpublished manuscript.

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Based on the comments and suggestions of the reviewers and editors a revision of the manuscript may be requested to the authors. A revised manuscript should be submitted by the authors, containing the changes made in the manuscript clearly highlighted. Responses to the reviewers must also be submitted answering in detail to the questions made by them, and describing the changes made in the manuscript.

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