

PS An Optimum Sample Preparation Method for Multi-element Analysis in Crude or Fuel Oils with ICP-OES and QQQ-ICP-MS by Mineralization Utilizing a Single-Reaction-Chamber Microwave System*

Weihang Yang¹, John F. Casey², and Yongjun Gao²

Search and Discovery Article #42142 (2017)**

Posted October 16, 2017

*Adapted from poster presentation given at AAPG 2017 Annual Convention and Exhibition, Houston, Texas, April 2-5, 2017

**Datapages © 2017 Serial rights given by author. For all other rights contact author directly.

¹Department of Earth and Atmospheric Sciences, University of Houston, Houston, Texas, United States (weihangy@hotmail.com)

²Department of Earth and Atmospheric Sciences, University of Houston, Houston, Texas, United States

Abstract

A sample preparation method was developed to accurately and precisely analyze up to 57 elements in crude oils and fuel oils by ICP-OES, used in tandem with QQQ-ICP-MS. To eliminate spectral and polyatomic interferences caused by the complex organic matrix of crude oils, we decomposed oil samples to form aqueous solutions using strong-acid digestions. Our test of many strong acid preparation techniques included combustion followed by digestion, Parr Bomb acid digestions, and single reaction chamber (SRC) microwave assisted acid digestions. A synthetic multi-element metallo-organic standard from Conostan Oil Analysis Standards (USA) was tested thoroughly for recovery of analytes by each digestion method. No element showed recovery above 75% in our best combustion test, whereas based on 5 replicate digestions, Parr Bomb average recoveries ranged from 94% to 106% for 19 elements in the standard and SRC microwave test average recoveries ranged from 93% to 113% for 19 elements in the standard as well. A drawback of the Parr method was a rather small sample sizes (0.1g), which placed limits on method detection limit (MDL) and method quantitation limit (MQL). Because of rapid sample throughput and the larger sample sizes (1.2g), SRC microwave digestion method was chosen to achieve better MDL and MQL on a range of elements. We then successfully tested SRC recovery (90-110%) for 57 elements in standards added to a Conostan base oil. The SRC technique was used to digest a NIST RM 8505 natural crude oil in an attempt to quantify up to 57 elements, based on 5 replicate digestions and analyses. We were able to precisely and accurately match the only recommended value referenced by NIST RM 8505 for vanadium, which is reported as 390±10 µg/g. Our result is 390±0.4 µg/g. We were able to precisely quantify 52 elements, with %RSDs of < 5% for 38 elements, 5-10% for 10 elements, and 10-15.6% for 4 elements, all meeting our acceptability limits of < 20% RSD. Successful quantification was achieved by ICP-OES for higher abundance elements and by QQQ-ICP-MS for low abundance elements using the SRC microwave-assisted preparation. B, Nb, and W, although above MQL, were judged unacceptable because their RSDs were > 31.4%, whereas Ag and Tl were below MQL, and their RSDs were > 44.2% and judged unacceptable as well; although these elements have been quantified in other natural crude oils.

Selected References

- Akinlua, A., T.R. Ajayi, and B.B. Adeleke, 2007, Organic and Inorganic Geochemistry of Northwestern Niger Delta Oils: *Geochemical Journal*, v. 41/4, p. 271-281.
- Akinlua, A., and N. Torto, 2006, Determination of Selected Metals in Niger Delta Oils by Graphite Furnace Atomic Absorption Spectrometry: *Analytical Letters*, v. 39/9, p. 1993-2005.
- Alberdi-Genolet, M., and R. Tocco, 1999, Trace Metals and Organic Geochemistry of the Machiques Member (Aptian-Albian) and La Luna Formation (Cenomanian-Campanian), Venezuela: *Chemical Geology*, v. 160/1, p. 19-38.
- Algeo, T.J., and H. Rowe, 2012, Paleooceanographic Applications of Trace-Metal Concentration Data: *Chemical Geology*, v. 324, p. 6-18.
- Algeo, T.J., and J.B. Maynard, 2004, Trace-Element Behavior and Redox Facies in Core Shales of Upper Pennsylvanian Kansas-Type Cyclothems: *Chemical Geology*, v. 206/3, p. 289-318.
- Amorim, F.A., B. Welz, A.C. Costa, F.G. Lepri, M.R.G. Vale, and S.L. Ferreira, 2007, Determination of Vanadium in Petroleum and Petroleum Products Using Atomic Spectrometric Techniques: *Talanta*, v. 72/2, p. 349-359.
- Aucélio, R.Q., A. Doyle, B.S. Pizzorno, M.L.B. Tristão, and R.C. Campos, 2004, Electrothermal Atomic Absorption Spectrometric Method for the Determination of Vanadium in Diesel and Asphaltene Prepared as Detergentless Microemulsions: *Microchemical Journal*, v. 78/1, p. 21-26.
- Balashov, Y.A., A.B. Ronov, A.A. Migdisov, and N.V. Turanskava, 1964, The Effect of Climate and Facies Environment on the Fractionation of the Rare Earths During Sedimentation: *Geochemistry International*, v. 5, p. 951-969.
- Barwise, A.J.G., 1990, Role of Nickel and Vanadium in Petroleum Classification: *Energy and Fuels*, v. 4/6, p. 647-652.
- Casey, J., Y. Gao, W. Yang, and R. Thomas, 2016, New Approaches in Sample Preparation and Precise Multielement Analysis of Crude Oils and Refined Petroleum Products Using Single-Reaction-Chamber Microwave Digestion and Triple Quadrupole ICP-MS: *Spectroscopy*, v. 31/10, p. 11-22.
- Curiale, J.A., 1987, Distribution and Occurrence of Metals in Heavy Crude Oils and Solid Bitumens - Implications for Petroleum Exploration. *Exploration for Heavy Crude Oil and Natural Bitumen: American Association of Petroleum Geologists Studies in Geology*, v. 25, p. 207-219.
- de Azevedo Mello, P., J.S.F. Pereira, D.P. de Moraes, V.L. Dressler, É.M. de Moraes Flores, and G. Knapp, 2009, Nickel, Vanadium and Sulfur Determination by Inductively Coupled Plasma Optical Emission Spectrometry in Crude Oil Distillation Residues After Microwave-Induced Combustion: *Journal of Analytical Atomic Spectrometry*, v. 24/7, v. 911-916.

de Souza, R.M., A.L. Meliande, C.L. da Silveira, and R.Q. Aucélio, 2006, Determination of Mo, Zn, Cd, Ti, Ni, V, Fe, Mn, Cr and Co in Crude Oil Using Inductively Coupled Plasma Optical Emission Spectrometry and Sample Introduction as Detergentless Microemulsions: *Microchemical Journal*, v. 82/2, p. 137-141.

Duyck, C., N. Miekeley, C.L.P. da Silveira, R.Q. Aucelio, R.C. Campos, P. Grinberg, and G.P. Brandao, 2007, The Determination of Trace Elements in Crude Oil and Its Heavy Fractions by Atomic Spectrometry: *Spectrochimica Acta Part B: Atomic Spectroscopy*, v. 62/9, p. 939-951.

Duyck, C., N. Miekeley, C.L.P. da Silveira, and P. Szatmari, 2002, Trace Element Determination in Crude Oil and Its Fractions by Inductively Coupled Plasma Mass Spectrometry Using Ultrasonic Nebulization of Toluene Solutions: *Spectrochimica Acta Part B: Atomic Spectroscopy*, v. 57/12, p. 1979-1990.

Ellis, J., C. Rechsteiner, M. Moir, and S. Wilbur, 2011, Determination of Volatile Nickel and Vanadium Species in Crude Oil and Crude Oil Fractions by Gas Chromatography Coupled to Inductively Coupled Plasma Mass Spectrometry: *Journal of Analytical Atomic Spectrometry*, v. 26/8, p. 1674-1678.

Ellrich, J., A. Hirner, and H. Stärk, 1985, Distribution of Trace Elements in Crude Oils from Southern Germany: *Chemical Geology*, v. 48/1, p. 313-323.

Greibrokk, T., E. Lundanes, H.R. Norli, K. Dyrstad, and S.D. Olsen, 1994, Experimental Simulation of Oil Migration - Distribution Effects on Organic Compound Groups and on Metal/Metal Ratios: *Chemical Geology*, v. 116/3-4, p. 281-299.

Hammond, J.L., Y.I. Lee, C.O. Noble, J.N. Beck, C.E. Proffitt, and J. Sneddon, 1998, Determination of Cadmium, Lead, and Nickel by Simultaneous Multielement Flame Atomic Absorption Spectrometry in Burned and Unburned Venezuelan Crude Oil: *Talanta*, v. 47/2, p. 261-266.

Haskin, L.A., T.R. Wildeman, F.A. Frey, K.A. Collins, C.R. Keedy, and M.A. Haskin, 1966, Rare Earths in Sediments: *Journal of Geophysical Research*, v. 71/24, p.6091-6105.

Hitchon, B., R.H. Filby, T.F. Yen, and K.R. Shah, 1975, *Geochemistry of Trace Elements in Crude Oils, Alberta, Canada*: Ann Arbor Science.

Jackson, B.P., A. Liba, and J. Nelson, 2015, Advantages of Reaction Cell ICP-MS on Doubly Charged Interferences for Arsenic and Selenium Analysis in Foods: *Journal of Analytical Atomic Spectrometry*, v. 30/5, p. 1179-1183.

Jin, H., S. Sonnenberg, and R. Sarg, 2015, Source Rock Potential and Sequence Stratigraphy of Bakken Shales in the Williston Basin. Unconventional Resources Technology Conference (URTEC).

Jones, B., and D.A. Manning, 1994, Comparison of Geochemical Indices Used for the Interpretation of Palaeoredox Conditions in Ancient Mudstones: *Chemical Geology*, v. 111/1-4, p. 111-129.

Kahen, K., A. Strubinger, J.R. Chirinos, and A. Montaser, 2003, Direct Injection High Efficiency Nebulizer-Inductively Coupled Plasma Mass Spectrometry for Analysis of Petroleum Samples: *Spectrochimica Acta Part B: Atomic Spectroscopy*, v. 58/3, p. 397-413.

Kelly, W.R., S.E. Long, and J.L. Mann, 2003, Determination of Mercury in SRM Crude Oils and Refined Products by Isotope Dilution Cold Vapor ICP-MS Using Closed-System Combustion: *Analytical and Bioanalytical Chemistry*, v. 376/5, p. 753-758.

Kuhawar, M.Y., M.A. Mirza, and T.M. Jahangir, 2012, Determination of Metal Ions in Crude Oils: INTECH Open Access Publisher.

Korn, M.D.G.A., D.S.S. dos Santos, B. Welz, M.G.R. Vale, A.P. Teixeira, D. de Castro Lima, and S.L.C. Ferreira, 2007, Atomic Spectrometric Methods for the Determination of Metals and Metalloids in Automotive Fuels - A Review: *Talanta*, v. 73/1, p. 1-11.

Kowalewska, Z., A. Ruszczyńska, and E. Bulska, 2005, Cu Determination in Crude Oil Distillation Products by Atomic Absorption and Inductively Coupled Plasma Mass Spectrometry After Analyte Transfer to Aqueous Solution: *Spectrochimica Acta Part B: Atomic Spectroscopy*, v. 60/3, p. 351-359.

Lewan, M.D., 1984, Factors Controlling the Proportionality of Vanadium to Nickel in Crude Oils: *Geochimica et Cosmochimica Acta*, v. 48/11, p. 2231-2238.

Lewan, M.D., and J.B. Maynard, 1982, Factors Controlling Enrichment of Vanadium and Nickel in the Bitumen of Organic Sedimentary Rocks: *Geochimica et Cosmochimica Acta*, v. 46/12, p. 2547-2560.

López, L., and S.L. Mónaco, 2004, Geochemical Implications of Trace Elements and Sulfur in the Saturate, Aromatic and Resin Fractions of Crude Oil from the Mara and Mara Oeste Fields, Venezuela: *Fuel*, v. 83/3, p. 365-374.

Lord III, C.J., 1991, Determination of Trace Metals in Crude Oil by Inductively Coupled Plasma Mass Spectrometry with Microemulsion Sample Introduction: *Analytical Chemistry*, v. 63/15, p. 1594-1599.

Meeravali, N.N., and S.J. Kumar, 2001, The Utility of a W-Ir Permanent Chemical Modifier for The Determination of Ni and V in Emulsified Fuel Oils and Naphtha by Transverse Heated Electrothermal Atomic Absorption Spectrometer. This paper is dedicated to the memory of the late Dr. S. Gangadharan, Ex-CE, CCCM-BRIT: *Journal of Analytical Atomic Spectrometry*, v. 16/5, p. 527-532.

Mello, P.A., J.S. Pereira, M.F. Mesko, J.S. Barin, and E.M. Flores, 2012, Sample Preparation Methods for Subsequent Determination of Metals and Non-Metals in Crude Oil - A Review: *Analytica Chimica Acta*, v. 746, p. 15-36.

Milestone Inc., Milestone Digestion Products. <http://www.milestonesci.com/digestion>. Website accessed October 2017.

Minami, E., 1935, Gehalte an seltenen Erden in europaischen and japanischen Tonschiefern. Nachr. Gess. Wiss. Gottingen, 2, Math-Physik. Kl. IV, 1, p. 155-170.

Nelson, J., G. Gilleland, L. Poirier, D. Leong, P. Hajdu, and F. Lopez-Linares, 2015, Elemental Analysis of Crude Oils Using Microwave Plasma Atomic Emission Spectroscopy: Energy and Fuels, v. 29/9, p. 5587-5594.

Noble, C.O., J.L. Hammond, J.N. Beck, C.E. Proffitt, and J. Sneddon, 1997, Direct Determination of Lead in Smoke from Burned Crude Oil by Impaction Graphite Furnace Atomic Absorption Spectrometry: Microchemical Journal, v. 57/3, p. 361-369.

Oluwole, A.F., O.I. Asubiojo, J.I. Nwachukwu, J.O. Ojo, O.J. Ogunsola, J.A. Adejumo, and C. Grimm, 1993, Neutron Activation Analysis of Nigerian Crude Oils: Journal of Radioanalytical and Nuclear Chemistry, v. 168/1, p. 145-152.

Ortega, G.S., C. Pécheyran, G. Hudin, E. Marosits, and O.F. Donard, 2013, Different Approaches of Crude Oil Mineralization for Trace Metal Analysis by ICPMS: Microchemical Journal, v. 106, p. 250-254.

Pereira, J.S., D.P. Moraes, F.G. Antes, L.O. Diehl, M.F. Santos, and R.C. Guimarães, 2010, Determination of Metals and Metalloids in Light and Heavy Crude Oil by ICP-MS After Digestion by Microwave-Induced Combustion: Microchemical Journal, v. 96/1, p. 4-11.

Pelizzetti, E., and E. Pramauro, 1985, Analytical Applications of Organized Molecular Assemblies: Analytica Chimica Acta, v. 169, p. 1-29.

Poirier, L., J. Nelson, D. Leong, L. Berhane, P. Hajdu, and F. Lopez-Linares, 2016, Application of ICP-MS and ICP-OES on the Determination of Nickel, Vanadium, Iron, and Calcium in Petroleum Crude Oils via Direct Dilution: Energy and Fuels, v. 30/5, p. 3783-3790.

Sánchez, R., J.L. Todolí, C.P. Lienemann, and J.M. Mermet, 2013, Determination of Trace Elements in Petroleum Products by Inductively Coupled Plasma Techniques: A Critical Review: Spectrochimica Acta Part B: Atomic Spectroscopy, v. 88, p. 104-126.

Sant'Ana, F.W., R.E. Santelli, A.R. Cassella, and R.J. Cassella, 2007, Optimization of an Open-Focused Microwave Oven Digestion Procedure for Determination of Metals in Diesel Oil by Inductively Coupled Plasma Optical Emission Spectrometry: Journal of Hazardous Materials, v. 149/1, p. 67-74.

Sedykh, E.M., L.N. Bannykh, G.S. Korobeinik, and N.P. Starshinova, 2011, Determination of Nickel and Vanadium in Crude Oils by Electrothermal Atomic Absorption Spectrometry and Inductively Coupled Plasma Atomic Emission Spectroscopy After Mineralization in an Autoclave: Inorganic Materials, v. 47/14, p. 1539-1543.

Sneddon, J., C.O. Noble, M.V. Smith, and J.N. Beck, 2004, Simultaneous Determination of Cadmium, Chromium, Lead, and Manganese in Smoke from Burning Oil by Impaction Graphite Furnace Atomic Absorption Spectrometry: *Spectroscopy Letters*, v. 37/2, p. 151-157.

Taylor S.R. and S.M. McLennan, 1985, *The Continental Crust: Its Composition and Evolution*: Blackwell, Oxford.

Thompsen, V., 2012, Spectral Background Radiation and the "Background Equivalent Concentration" in Elemental Spectrochemistry: *Spectroscopy*, v. 27/3, p. 28-36.

Tribovillard, N., T.J. Algeo, F. Baudin, and A. Riboulleau, 2012, Analysis of Marine Environmental Conditions Based On molybdenum - Uranium Covariation - Applications to Mesozoic Paleoceanography: *Chemical Geology*, v. 324, p. 46-58.

Tribovillard, N., T.J. Algeo, T. Lyons, and A. Riboulleau, 2006, Trace Metals as Paleoredox and Paleoproductivity Proxies: An Update: *Chemical Geology*, v. 232/1, p. 12-32.

Walkner, C., R. Gratzner, T. Meisel, and S.N.H. Bokhari, 2017, Multi-Element Analysis of Crude Oils Using ICP-QQQ-MS: *Organic Geochemistry*, v. 103, p. 22-30.

Wondimu, T., and W. Goessler, 2000, Comparison of Closed-Pressurized and Open-Refluxed Vessel Digestion Systems for Trace Elements in the Residual Fuel Oil Reference Material (SRM 1634c): *Bulletin of the Chemical Society of Ethiopia*, v. 14/2, p. 99-113.

Wondimu, T., W. Goessler, and K.J. Irgolic, 2000, Microwave Digestion of "Residual Fuel Oil" (NIST SRM 1634b) for the Determination of Trace Elements by Inductively Coupled Plasma-Mass Spectrometry: *Fresenius' Journal of Analytical Chemistry*, v. 367/1, p. 35-42.



An Optimum Sample Preparation Method for Multi-element Analysis in Crude or Fuel Oils with ICP-OES and QQQ-ICP-MS by Mineralization Utilizing a Single-Reaction-Chamber Microwave System



Weihang Yang (wyang6@uh.edu), John F. Casey, and Yongjun Gao
Department of Earth and Atmospheric Sciences, University of Houston

Introduction

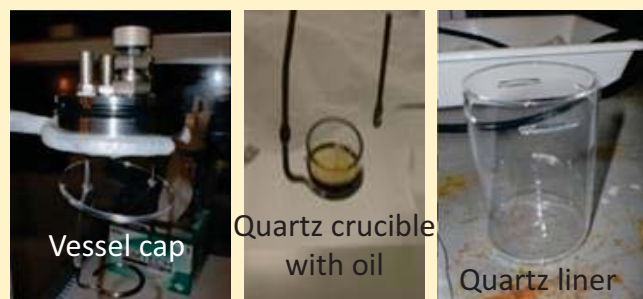
- Concentrations and ratios of trace metal elements have been used to understand oil formation, e.g., for oil-oil correlations and oil source rock correlations, oil migration, maturation of organic matter, and the depositional environment of source rocks, and for allowing corrective performance during crude oils processing and environmental risk evaluation.
- Crude oil samples need pretreatment preparation prior to being introduced into many analytical instruments (including ICP-OES and ICP-MS) because of their complex composition that have deleterious instrumental effects and severity of, for example, carbon-based analyte interferences.
- Four sample preparation methods have been mainly used for crude oil samples: (1) mineralization by strong acid digestion; (2) mineralization by combustion; (3) direct crude oil introduction after dilution with organic solvent; (4) direct emulsion/micro-emulsion introduction.
- This study was to develop a sample preparation method to accurately and precisely analyze multiple elements (up to 57) in crude oils.
- We chose to test and judge the best digestion method from mineralization by combustion, Parr bomb strong acid digestion, and SRC (Single Reaction Chamber) microwave strong acid digestion, because the higher MQL (Method Quantitation Limit) and MDL (Method Detection Limit) as a consequence of large dilution (e.g., $\times 100$, $\times 1,000$) keep direct introduction methods from analyzing a wide range of trace and ultra-trace elements for complete chemical fingerprints.

Experimental & Analytical Techniques

- 1.) A 350 ml general-purpose oxygen combustion vessel (Model 1108) from Parr Instrument Company (USA) was used for the closed vessel and high pressure combustion test.



Figure 1. The oil sample inside the oil combustion vessel was ignited by an ignition unit (Model 2901 EB) that was connected to the vessel. The unit ignited the vessel by electrifying it. The combustion procedure is conducted inside a Covered Quartz Liner to prevent sample loss. vessel safely burns sample using oxygen charging pressures up to 40 atm. Generally, the maximum combustible material size is 1,100 mg of oil.



- 2.) Fifteen 23 ml general purpose acid digestion vessels (Model 4749) from Parr Instrument Company were used for the closed vessel and high pressure acid digestion test.



Figure 2. Operating temperatures and pressures up to a maximum of 250 °C and 1,800 psig are permitted in this vessel using a thick-walled PTFE liner. The maximum acceptable organic sample size is 100 mg to prevent venting based on our tests.

- 3.) The Single Reaction Chamber (SRC) Microwave Digestion System (UltraWAVE) from Milestone, Inc. (USA), operating at a maximum power supply of 1,500 W, was used for the closed reaction chamber, high temperature, and high pressure acid digestion test.

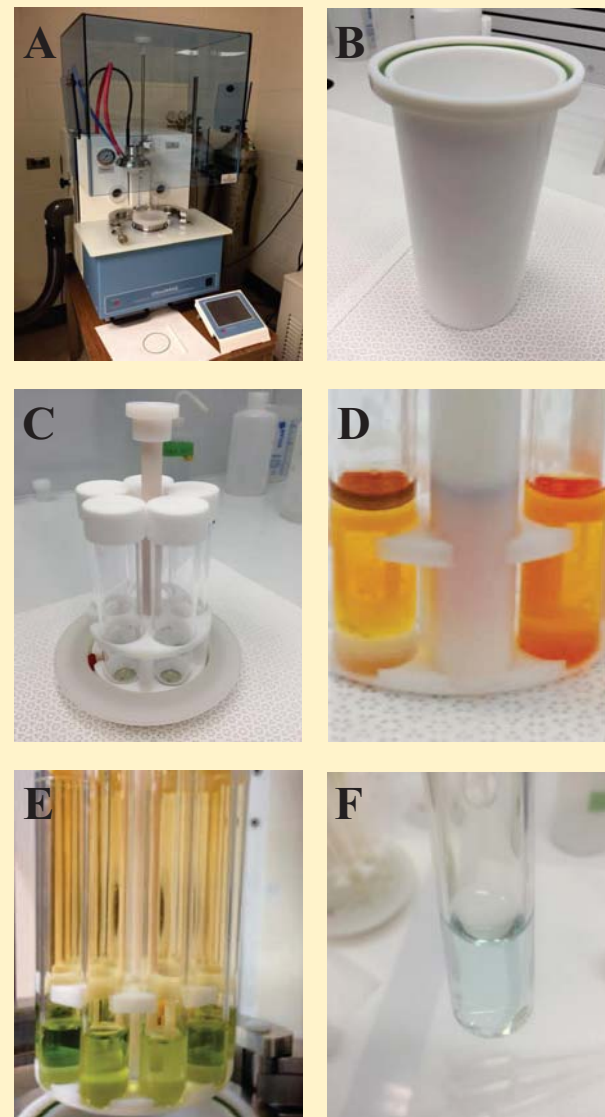


Figure 3. Summary of an SRC microwave digestion system. A: SRC microwave digestion system (Model UltraWAVE from Milestone, Inc); B: PTFE liner used to contain base load of 130 ml of Milli-Q water and 5 ml of 16N HNO₃; C: 40 ml quartz tubes held by a rack used to contain oil samples and mixes of digestion reagents; D: initial oil samples floating on the surface of mixes of digestion reagents because oil is less dense than mixes of digestion reagents (Casey et al., 2016); E: digested oil samples in aqueous form with NO_x dissolved because 16N HNO₃ is a digestion reagent (Casey et al., 2016); F: digested oil samples in aqueous form after degassing of NO_x, which will occur after the digested oil samples stand for a few hours.

- A QQQ-ICP-MS (Model 8800) and an ICP-OES (Model 725) from Agilent Technologies (USA) were used to analyze the concentration of trace elements.



Figure 4. ICP-OES (Model 725) from Agilent Technologies (US). Instrumental detection limit (IDL) is about 2 ng/g commonly. Therefore, it was used for high abundance trace elements determination.



Figure 5. QQQ-ICP-MS (Model 8800) from Agilent Technologies (US). IDL can be as low as 0.02 pg/g, commonly around 1 pg/g. Therefore, it was used for low abundance trace elements determination.



Figure 6. The acids (HNO₃ and HCl) used in this study were purified by Milestone subCLEAN, which is an easy-to-use sub-boiling system. The distillation rate is about 2 times faster than traditional two bottle distillation setup while can produce a superb clean acid due to its fully enclosed design.

Method Development

- For combustion method, no element showed recovery above 75%, thus this method was deemed unacceptable for accurate and precise analysis of crude oil.
- Average recoveries ranging from 94% to 106% for 19 analytes were achieved with high pressure and high temperature acid digestion within Parr bombs, with a drawback of small sample size of only 0.1 g.

- The best of the SRC microwave assisted acid digestion tests was also shown to be acceptable for 19 analytes with average recoveries ranging from 93% to 113%.

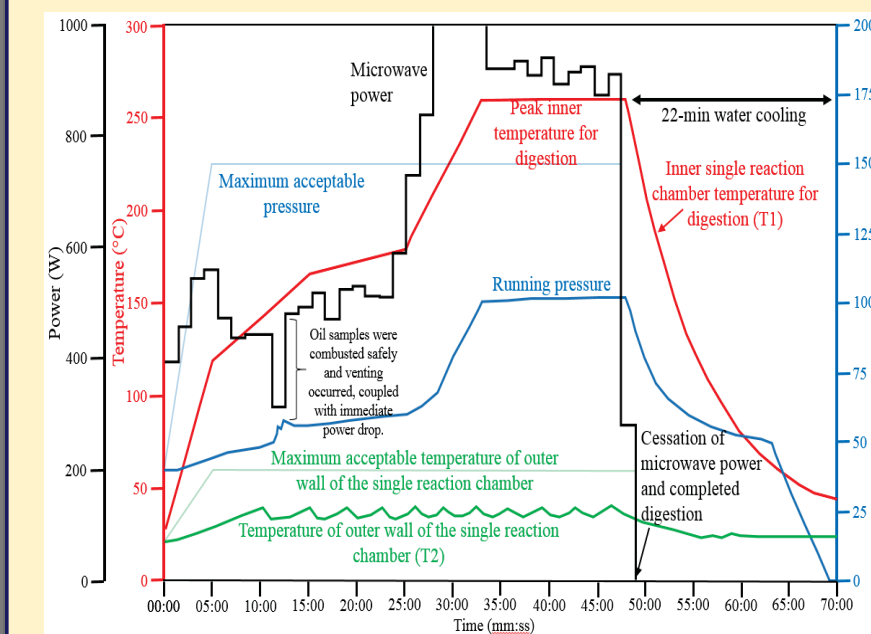


Figure 7. Plot of data file of power, temperature, and pressure against time using a SRC microwave digestion system.

- The mineralization efficiency was successfully tested to be approximately 100%. RCCs (residual carbon contents) of 9 crude oil samples range from 14.9% to 18.9%, with less than 0.1% in analyzed solutions.



Figure 8. CS 230 Carbon Sulfur Analyzer.

- RCC (%) = (Cf (%) × Mf (g)) / (Cs (%) × Ms (g)) (Sant'Ana et al., 2007). Cf: carbon content in digested solution, Mf: mass of solution, Cs: carbon content in crude oil sample, Ms: mass of crude oil sample.

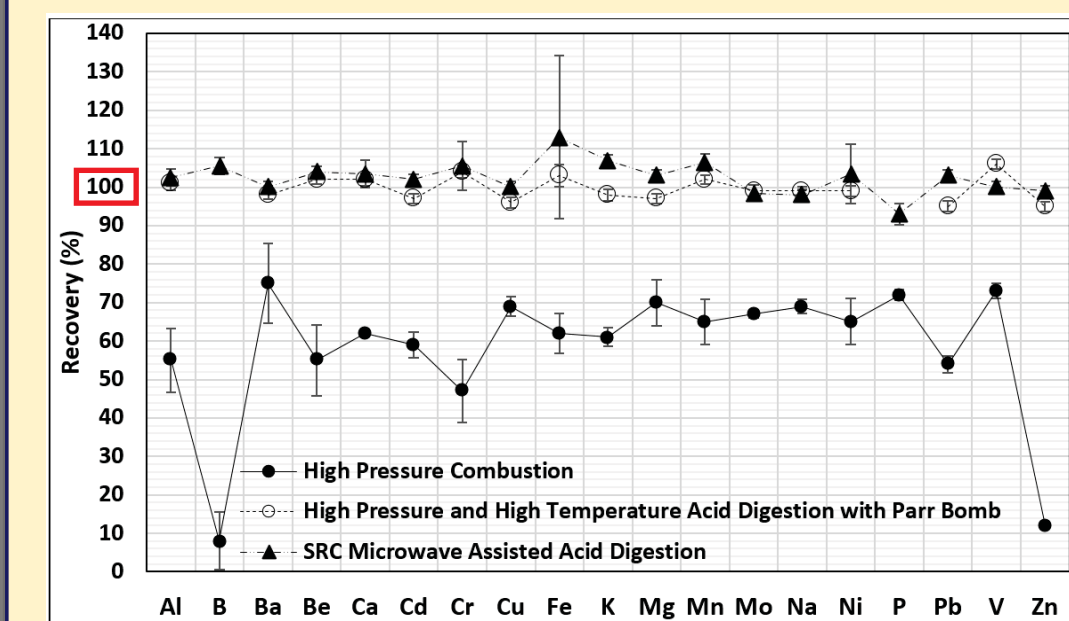


Figure 9. Summary of the best test recoveries of 19 out of 24 analytes of the three sample preparation methods, i.e., Parr combustion, Parr high pressure bombs, and SRC microwave.

- The developed SRC microwave assisted experimental protocol was first tested by a doping experiment for up to 57 elements.

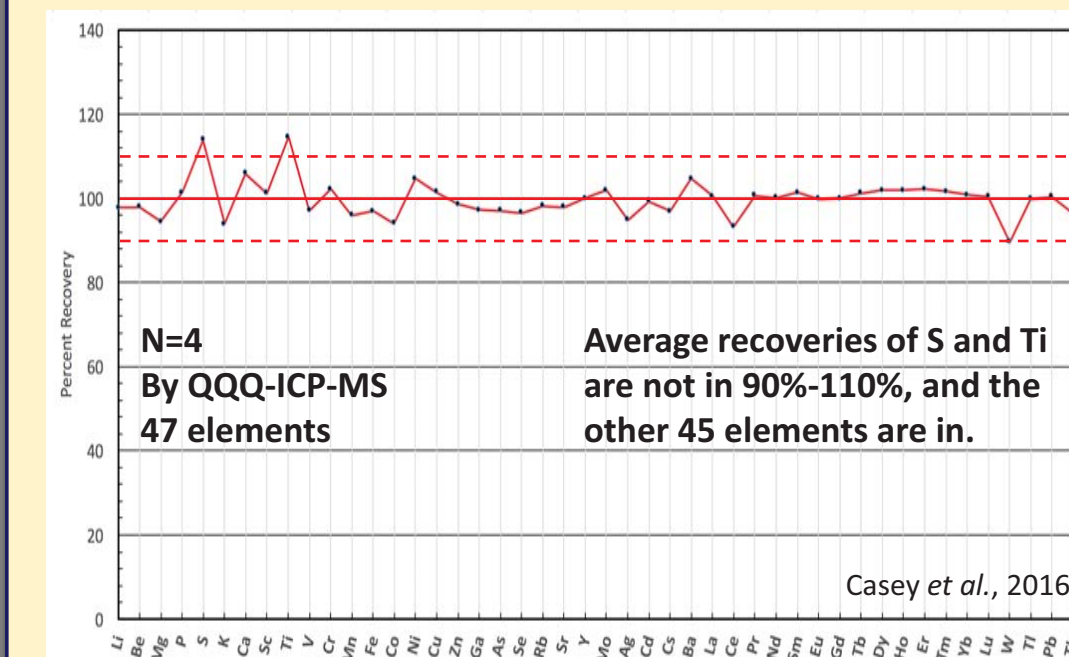


Figure 10. Doping Recovery Test - 500 ng of each analyte was added into 400 mg of blank oil (Conostan).

Test of NIST RM 8505

- The developed microwave assisted experimental protocol was used to test a natural crude oil reference material NIST 8505 for up to 57 elements.

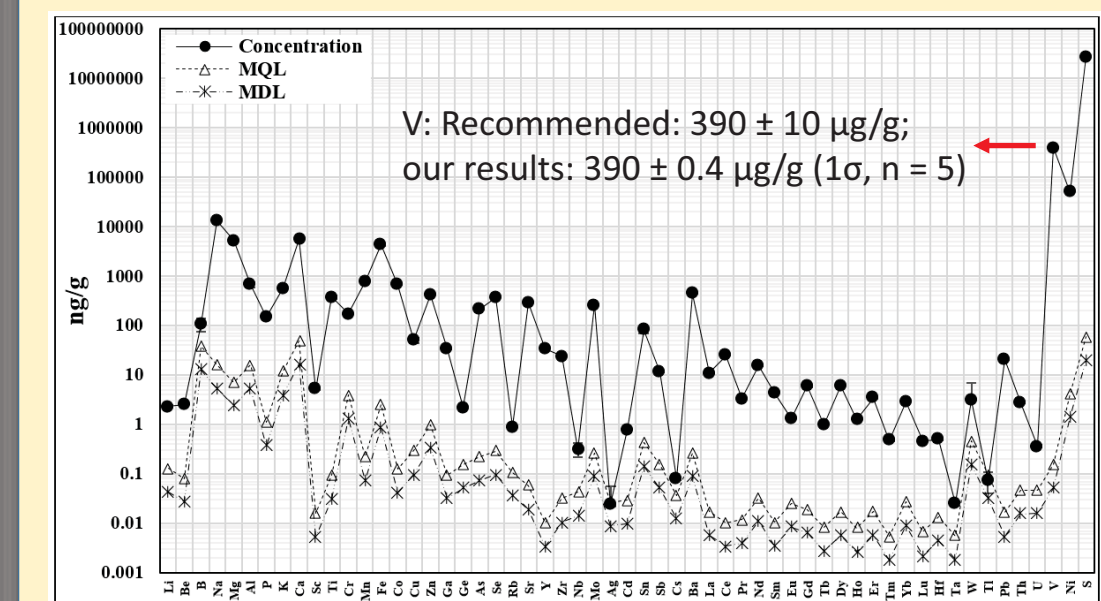


Figure 11. Analytical results of all the 57 tested elements in the natural crude oil reference material NIST 8505 using SRC microwave assisted high pressure and high temperature acid digestion.

- The analytical results of rare earth elements + Yttrium (REY) were normalized to Post-Archean Australian Shale (PAAS) to see their relationship.

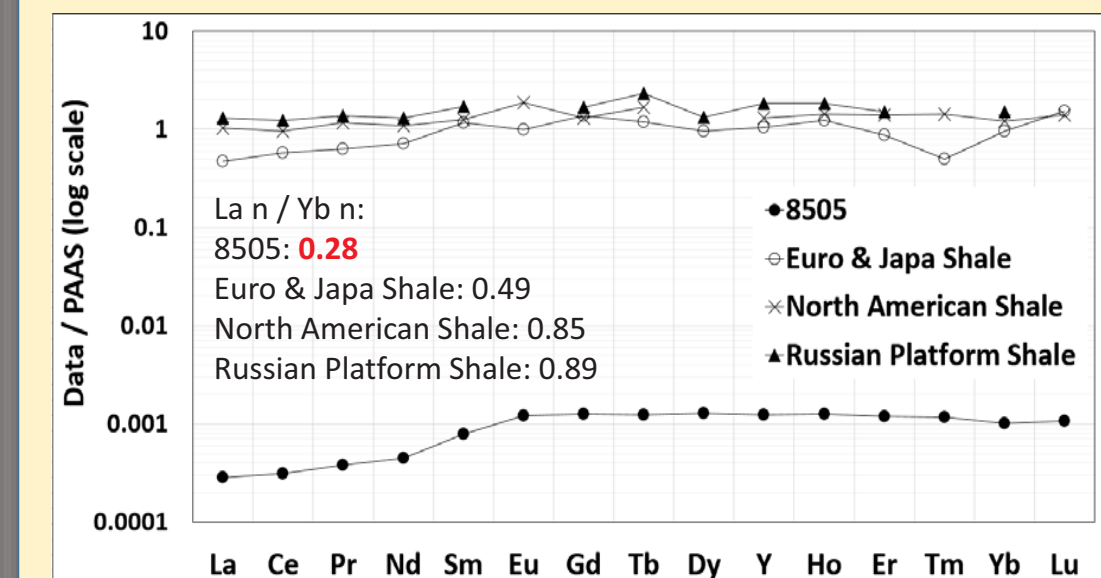


Figure 12. PAAS "Shale" [Taylor and McLennan (1985)] normalized REY pattern indicating depletion of LREE of NIST RM 8505. European and Japan shale [Minami (1935)], North American shale [Haskin et al. (1965b)], and Russian Platform shale [Balashov et al. (1964)] also shown for comparison.

Conclusions

- A method to accurately and precisely determine a broad range of elements in crude oil using ICP instruments was developed.
- The combustion method tests has considerable loss of all the analytes, thus were judged unacceptable.
- Test of high pressure and high temperature acid digestion with Parr bomb achieved recoveries of close to 100% for 19 out of 24 elements, with a sample size limit of only 0.1 g.
- The SRC microwave assisted acid digestion also obtained recoveries of around 100% for 19 elements. Rapid sample throughput and larger sample sizes (up to 0.4 g) make SRC microwave digestion the optimum method.
- The test of NIST RM 8505 using the developed optimum method yielded RSDs better than 15.6% for 52 tested elements, with 38 of them better than 5%. Our results for vanadium: 390 ± 0.4 µg/g, recommended value: 390 ± 10 µg/g.
- LREE of NIST RM 8505 is depleted based on the PAAS "Shale" normalized REY pattern.

References

- Casey, J., Gao, Y., Yang, W., & Thomas, R. (2016). New Approaches in Sample Preparation and Precise Multielement Analysis of Crude Oils and Refined Petroleum Products Using Single-Reaction-Chamber Microwave Digestion and Triple Quadrupole ICP-MS. *Spectroscopy*, 31(10), 11-22.
- Khuhawar, M. Y., Mirza, M. A., & Jahangir, T. M. (2012). Determination of metal ions in crude oils. *INTECH Open Access Publisher*.