National Technical University of Athens

EnvCRM

EMPIR EURAMET

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

EVALUATİON OF METHODS FOR THE DETERMİNATİON OF AQUA REGİA EXTRACTABLE TRACE ELEMENTS İN SOİLS

M. Ochsenkühn-Petropoulou[1] ,
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and F. Tsopelas[1]

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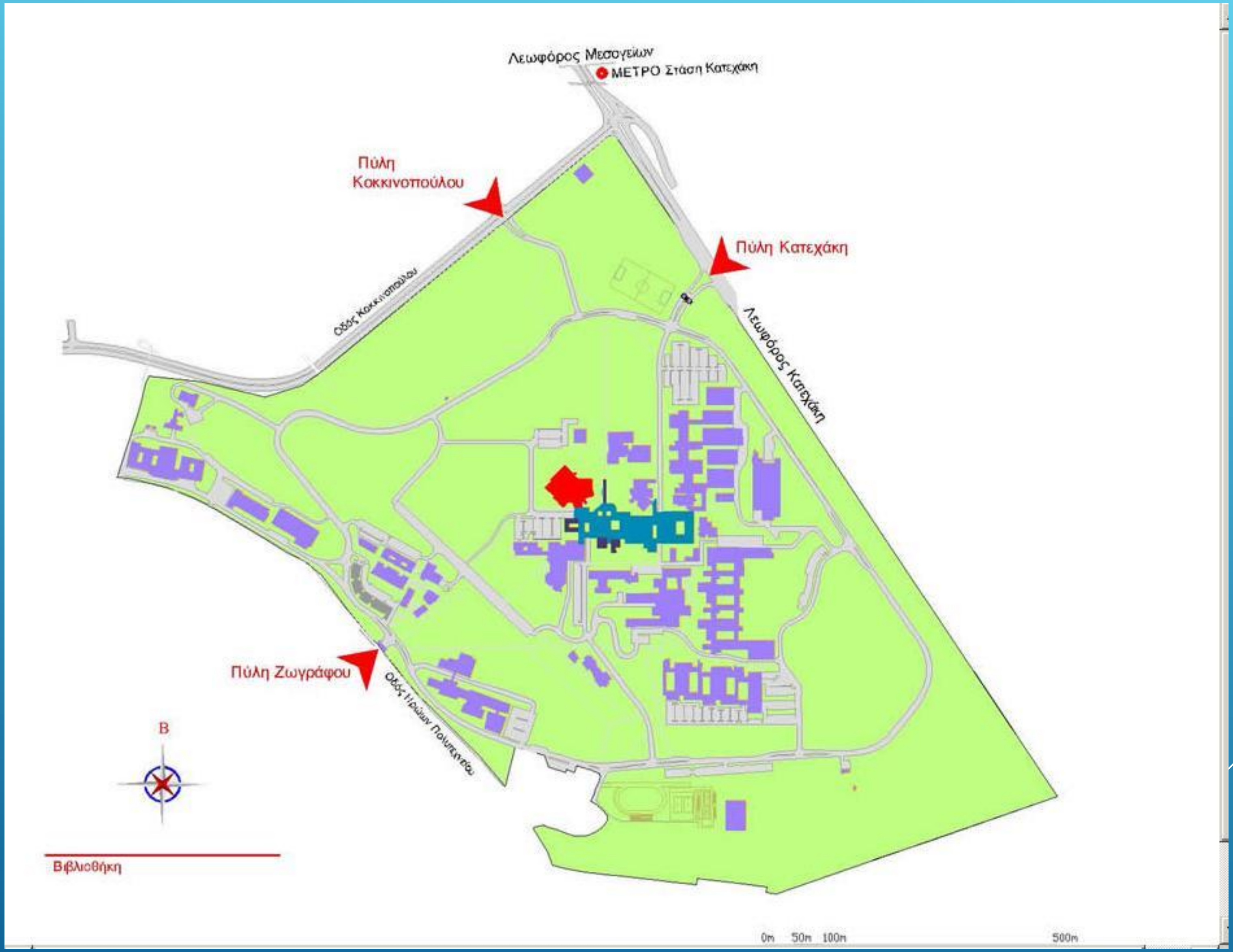
ENVCRM: Matrix Reference Materials for Environmental Analysis
WORKSHOP ON REFERENCE MATERIALS, TUBITAK UME , Gebze Turkey , 16/05/2018

NATIONAL TECHNICAL UNIVERSITY OF ATHENS: HISTORY

The National Technical University of Athens (NTUA) is the oldest and most prestigious educational institution of Greece in the field of technology.

It is linked to the country's scientific, technical and economic development since its **foundation in 1836** as well as to democracy and social progress.

The Campus of the NTUA



The NTUA in numbers

National
Technical
University of
Athens

Academic staff: 650
Total NTUA Employees: 1.350
Undergraduate students: 10.000
Postgraduate Students: 3.000
Schools: 9

- **School of Chemical Engineering**
- School of Civil Engineering
- School of Mechanical Engineering
- School of Electrical and Computer Engineering
- School of Architecture
- School of Rural and Surveying Engineering
- School of Mining Engineering and Metallurgy
- School of Naval Architecture and Marine Engineering
- School of Applied Mathematics and Physical Science

SCHOOL OF CHEMICAL ENGINEERING NTUA: LABORATORIES

The Laboratories of the School are distributed among the four Departments

I. Department of Chemical Sciences:

- Laboratory of Inorganic and Analytical Chemistry
- Laboratory of General Chemistry
- Laboratory of Organic Chemistry

II. Department of Process Analysis and Plant Design (e.g. Laboratory of Thermodynamics and Transport Phenomena, Chemical Process Engineering)

III. Department of Materials Science and Engineering (Laboratory of Physical Chemistry)

IV. Department of Synthesis and Development of Industrial Process (e.g. Laboratory of Biotechnology, Food Chemistry and Technology)

SCHOOL OF CHEMICAL ENGINEERING
LABORATORY OF INORGANIC AND ANALYTICAL CHEMISTRY
UNIT OF INSTRUMENTAL METHODS OF ANALYSIS-ENVIRONMENT

- Chemical analysis
  - inorganic analytes
  - metal speciation

- Environmental investigations

- EN ISO 9001:2008 in "Developing and conducting chemical analyses and environmental studies"

Prof. M. Ochsenkühn- Petropoulou, Prof. F. Tsopelas, Dr K.M. Ochsenkühn, Dr L.A. Tsakanika, Dr T. Lymperopoulou, Dr O.Serifi, Ch. Stergiopoulos (PhD student)

RESEARCH FIELDS

- Speciation Analysis, especially of tin, selenium and arsenic in environmental and biological matrices. Contribution to the production of CRMs. Participation in inter-comparison and certification exercises for the EC (ongoing EMPIR EURAMET project ENVCRM: Matrix reference materials for environmental analysis")
- Utilization of industrial byproducts. Extraction of scandium and lanthanides from red mud in laboratory and pilot-plant scale (ongoing Horizon 2020 project SCALE: "Production of Scandium compounds and Scandium Aluminum Alloys from European metallurgical byproducts")
- Air pollution: Airborne particulates in the Attica basin. Automobile Catalysts and Platinum Group Element Emissions. Wood pellets and particulate matter emissions. AEROSOL METROLOGY (ongoing EMPIRE EURAMET project AEROMET: Aerosol metrology for atmospheric science and air quality)
- Trace element analysis by voltammetric, spectroscopic and hyphenated chromatographic techniques
- Production and Characterization of powders and coatings of superconductors (YBCO, BSCCO, MgB_2)
- Analytical methods for the evaluation of biological properties of organo-metallic compounds and candidate drugs

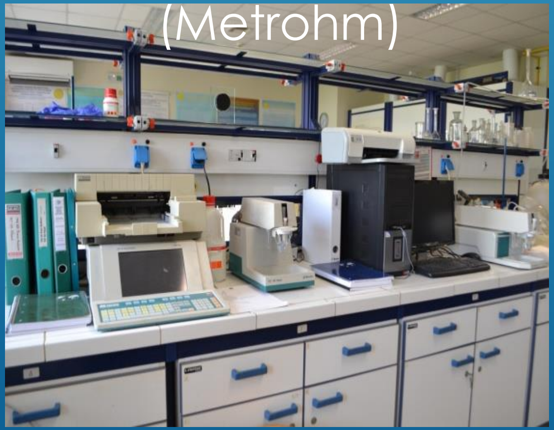
INSTRUMENTATION OF THE UNIT OF INSTRUMENTAL METHODS OF ANALYSIS- ENVIRONMENT

ICP-MS (Agilent)

HPLC (Perkin- Elmer)

AAS/GFAAS(Varian)

Voltammeric analyzer (Metrohm)



FTIR (Jasco)

Pilot plant

CENTER OF ENVIRONMENT AND QUALITY OF LIFE

It is a joint laboratory unit of the School of Chemical Engineering, equipped with high cost scientific instruments. It cooperates with the unit “Instrumental Methods of Analysis- Environment”.

LC-MS-MS

GC-MS

SEM

ICP-OES

XRD

XRF

RELATED TO THE PROJECT RESEARCH FIELDS

- A. Speciation Analysis (Se, As and Sn speciation) in food, environmental and biological samples. Certified reference materials
- B. Aerosol Metrology (EMPIR project AEROMET, on going). Air pollution: Airborne particulates in the Attica basin. Automobile Catalysts and Platinum Group Element Emissions. Wood pellets and particulate matter emissions
- C. Analytical methods for the evaluation of biological properties of organometallic compounds and candidate drugs. Ecotoxicological profile of environmental pollutants

A1. CRMS FOR SPECIATION ANALYSIS

- Development of analytical approaches for Se, As and Sn speciation based on selective extraction- ion exchange, liquid chromatography and detection with spectrometric and electro-analytical techniques
- Applications to environmental samples (water/ seawater, soil and sediments, marine organisms), food and biological samples
- Participation in inter-comparison exercises for the development of certified reference materials for As, Se and Sn

TIN SPECIATION IN SEDIMENT (INTERCOMPARISON EXERCISE)

Sample: Freshwater sediment CRM No 646 of Bureau of Reference Communities (BCR).

Analytical Approach: Leaching with 0.5 M HCl → Quantitative recovery of dibutyltin (DBT) and triphenyltin (TPT). Detection with voltammetric techniques.

Species	Results (ng Sn·g^{-1} dry sediment)		Deviation (%)
	NTUA	Mean value of intercomparison exercise	
DBT	270.0 ± 38.1	301.2 ± 45.8	- 10.3
TPT	9.8 ± 1.3	10.8 ± 1.6	- 9.2

K.M.Ochsenkuehn,M Ochsenkuehn-Petropoulou, F.Tsopelas, L.Mendrinos "Different Behavior of organotin compounds by anodic stripping voltammetry and their quantification after partial ion exchange separation" Mikrochim Acta 136(2001)129-135

ARSENIC SPECIATION IN SOIL CANDIDATE REFERENCE MATERIAL
("SEAS Project"/ INTERCOMPARISON EXERCISE)

Sample: Candidate Reference Material ***Soil IPL-1***

Analytical Approach: Leaching with conc. HCl → Quantitative recovery of As species. Detection with ICP-OES and HG-ICP-OES.

As species	**Results: μg As/ g dry sample**		**Deviation (%)**
	NTUA (ICP-OES, HG-ICP-OES)	**Mean value of intercomparison exercise**	
Total As	606 ± 18	613 ± 12	-1.1
As(III)	17 ± 5	18 ± 4	-5.6
As(V)	496 ± 21	514 ± 20	-3.5
MMA	65 ± 24	61 ± 23	+6.6
DMA	67 ± 23	64 ± 7	+4.7

SELENIUM SPECIATION IN YEAST CANDIDATE REFERENCE MATERIAL
("SEAS Project"/ INTERCOMPARISON EXERCISE)

Analytical Approach: Enzymatic extraction with Protease XIV→ Analysis with HPLC combined with ICP-OES detector.

Se Species	NTUA (μg Se/g dry sample)	SEAS Mean value (μg Se/g dry sample)	Deviation (%)
Total Se	1368.6 ± 46.5	1373.8 ± 101.5	-0.4
Se-Met	906.1 ± 25.6	873.9 ± 100.0	3.7
Se(IV)	22.2 ± 4.4	23.1 ± 14.8	-3.9

F.Tsopelas, M.Ochsenkuehn-Petropoulou, I.Mergias, L.Tsakanika " Comparison of ultra-violet and inductively coupled plasma-atomic emission spectrometry for the on-line quantification of selenium species after their separation by reversed-phase liquid chromatography" Anal Chim Acta 539 (2005)327-333

B.1.AEROSOL METROLOGY EMPIR AEROMET PROJECT

www.aernews-events/ometproject.com/

AEROMET
Aerosol metrology for atmospheric science and air quality

Motivation:

EU air quality regulations, climate change effects

Aim

- Improvement of uncertainty in particle mass, size and number
- Development of methods (mobile XRF) for in situ characterization of elements. Comparison with conventional methods

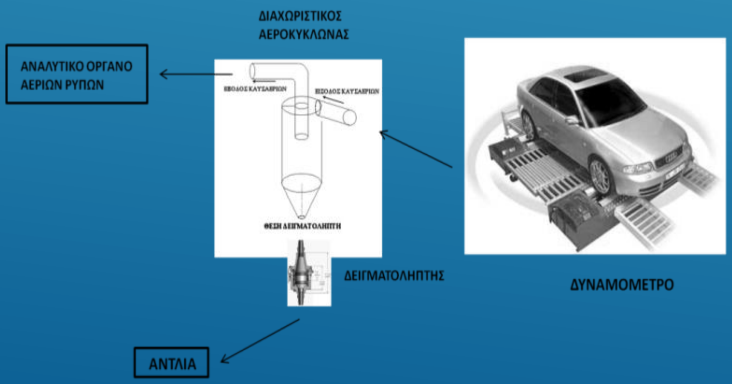
Begin: June 2017, End: May 2020

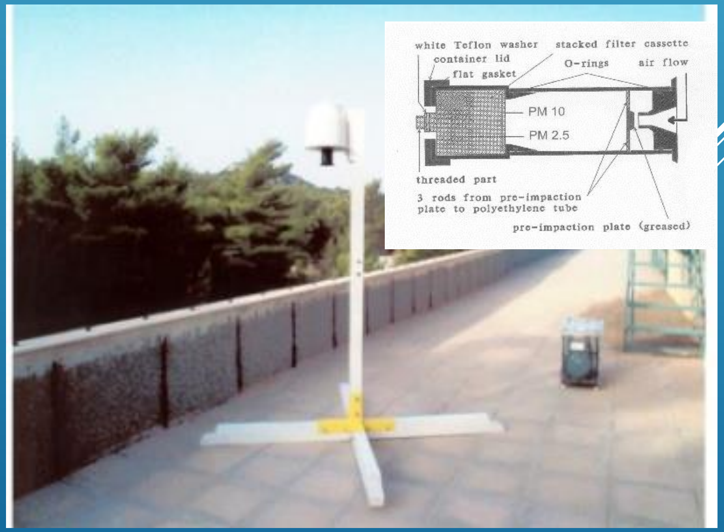
Members of AEROMET project

Internal Funded Partners:	External Funded Partners:	Unfunded Partners:
1 PTB, Germany	9 CIEMAT, Spain	20 Bruker, Germany
2 BAM, Germany	10 DTI, Denmark	21 METAS, Switzerland
3 CMI, Czech Republic	11 FORCE, Denmark	
4 DFM, Denmark	12 IRSN, France	
5 INRIM, Italy	13 JSI, Slovenia	
6 LNE, France	14 LUND, Sweden	
7 NILU Norway	15 MTA EK, Hungary	
8 NPL, United Kingdom	16 NTUA, Greece	
	17 TROPOS, Germany	
	18 UNICAS, Italy	
	19 UPO, Italy	

B2. AIR POLLUTION

- Qualitative and quantitative analysis (heavy metals, organic species, ions) of filters from aerosol samples(PM10/PM2.5). Identification of pollution sources
- Platinum Group Element Emissions from Automobile Catalysts: Development of a novel sampling system at the exhaust pipe of vehicles. Determination of platinum group elements by voltammetric techniques using ion-exchange separation/ preconcentration and GFAAS/ICP-MS
- Particulate matter emissions from combustion of different types of wood pellets





INTERLABORATORY PROFICIENCY TESTS SCHEMA (SCHEME FOR CHEMICAL MEASUREMENT ASSESSMENT)

SCHEMA	Title	Elements
03 01	Determination of Cd and Pb migration in ceramic articles	Cd, Pb
22 01	Determination of heavy elements in drinking waters	Cd, Pb, Cr, Cu, Ni, As, Sb, Al, Mn, Fe
62 01	Determination of heavy metals in foodstuffs (tea leaves, potato)	Cd, Pb, Cr (tot), Cr (VI), Cu, Ni, As

CRM PROJECTS - PROFICIENCY TESTS

- ✓ EMPIR Metrology Project AEROMET (AEROSOL METROLOGY FOR ATMOSPHERIC SCIENCE AND AIR QUALITY) Coordinator : PTB (2017-2020)
- ✓ EMPIR Metrology Project ENVCRM (Matrix Reference Materials for Environmental Analysis) Coordinator: TUBITAK (2015-2018)
- ✓ Interlaboratory proficiency tests SCHEMA (Scheme for Chemical Measurements

  Assessment) (2009-2012)
- ✓ Feasibility studies for speciated CRMs for arsenic in chicken, rice, fish, soil and selenium in yeast and cereal, "SEAS Project" (2001), EC Contract Ref: G6RD, CT 2001 (Coordinator: University of Plymouth)
- ✓ Measurements and Testing Programme (1995-1999): Certified reference materials: butyl- and phenyl- tin compounds in mussel and sediment (BCR), EU Project MAT 1-CT 94-071. Coordinator: Institute for Environmental Studies/ IVM Vrije Universiteit, Amsterdam
- ✓ Measurements and Testing Programme (1990-1994): Arsenic speciation project No. 336, Bureau of Reference Communities (BCR)
- ✓ Measurements and Testing Programme (1989-1993): Butyltin speciation Project No. 313, Bureau of Reference Communities (BCR)

A2. ENVCRM ACTIVITIES OF NTUA

EXTERNAL PARTNER

- Candidate CRMs for inorganic analytes:
  - soil candidate CRM: (As, Cd, Cr, Hg, Pb, Ni, Fe, Co, Mn, Cu, Zn, V, Sb) (13 elements)
  - river water CRM: (As, Cd, Hg, Ni, Pb) (5 elements) concentration levels from **μg/g** to sub **ng/g**
- Development and validation of reference digestion/leaching techniques and measurement by different analytical methods for the characterization of inorganic analytes in the soil candidate CRM.
- Analysis and validation of water candidate CRM by different

  analytical techniques (ICP-MS, ICP-OES, ASV)
- Calculation of the overall uncertainties
- Creating IMPACT. Organization of target meetings (IMA Conferences)

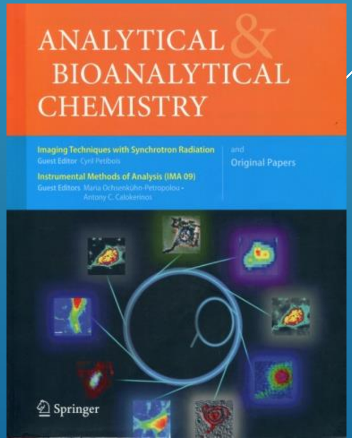
OTHER ACTIVITIES OF NTUA CREATING IMPACT

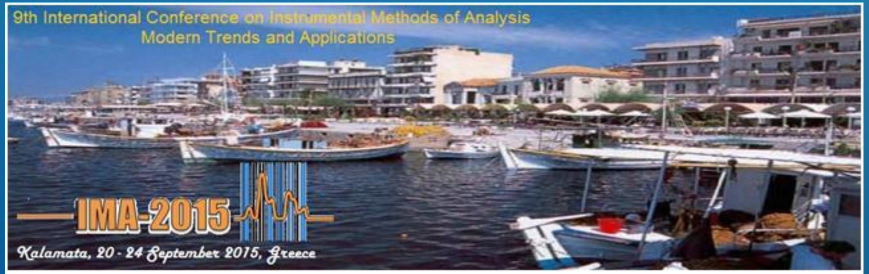
- ❑ Founding and organization of the biannual International **Conferences Instrumental Methods of Analysis-Modern Trends and Applications, IMA** (1999- 2015). Chairperson: 1999, 2009, 2013, 2015, 2017
- ❑ Guest editor in **Analytical and Bioanalytical Chemistry** (special issue for IMA 2009 and I


10th International Conference on
Instrumental Methods of Analysis
Modern Trends and Applications
Heraklion, September 17-21, 2017
IMA-2017
www.ima2017.gr


IMA 2011
The 7th International Conference on
Instrumental Methods of Analysis
Modern Trends and Applications
18-22 Sept. 2011, Chania Crete, GREECE


IMA-2013
8th International Conference on
Instrumental Methods of Analysis
Modern Trends and Applications
15-19 SEPTEMBER 2013
Thessaloniki, Greece


ANALYTICAL & BIOANALYTICAL CHEMISTRY
Imaging Techniques with Synchrotron Radiation
Guest Editor Cyril Petibois
Instrumental Methods of Analysis (IMA 09)
Guest Editors Maria Ochsenkühn-Petropolou • Antony C. Calokerinos
and
Original Papers
Springer


9th International Conference on Instrumental Methods of Analysis
Modern Trends and Applications
IMA-2015
Kalamata, 20 - 24 September 2015, Greece

A Joint Research Project for the Production and Certification of Matrix Reference Materials for Environmental Analysis

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M. HORVAT[6], A. ZOŃ[7], E. BULSKA[8], M. OCHSENKÜHN- PETROPOULOU[9],
S. Z. CAN[1], M. BİLSEL[1], K. HAFNER[4], N. PERKOLA[5], B. ARI[1], M. TUNÇ[1], B. BİNİCİ[1]

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[2]BAM-Federal Institute for Materials Research and Testing-GERMANY
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[4]IMBIH- Institute of Metrology-BOSNIA and HERZEGOVINA
[5]SYKE-Finnish Environment Institute-FINLAND
[6]IJS-Institute Jozef Stefan-SLOVENIA
[7]GUM-Central Office of Measures-POLAND
[8]UWAR-University of Warsaw-POLAND
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E-mail: alper.isleyen@tubitak.gov.tr

Reliable analysis of chemical indicators in water, sediment and soil samples for the purpose of environmental pollution assessment poses one of the greatest analytical challenges, having in mind the complexity of sample matrix and low concentrations of pollutants. Organics (pesticides, PAHs, PCBs, etc.) and heavy metals (Hg, Cd, Ni, Pb and As) represent target parameters.

Laboratories performing sampling and tests in this field regulated by respective EU directives [1], need strong support in terms of providing them with appropriate matrix CRMs enabling the process of quality control. NMIs and DIs with proven metrological capabilities for the production and certification of such materials are necessary for the provision of quality data.

This project is aiming to develop capacity to produce CRMs for environmental analysis by transferring the theoretical and practical know-how between the partners and combining their skills to focus on environmental CRM production in accordance with ISO Guide 34 [2].

Production process includes good manufacturing practices for processing materials, method development and validation for homogeneity, stability and characterisation tests, characterisation of selected analytes together with additional information about matrix constituents, the calculation of individual uncertainties (between units inhomogeneity, long term stability, characterisation) and combination of uncertainties to determine overall uncertainty of the matrix reference materials. Inter laboratory comparison registered as EURAMET project is set as the ultimate project outcome, confirming the partners' capabilities in applying newly acquired skills.

References

[1] Water Framework Directive 2008/105/EC – Annex II: Priority substances and other pollutants- http://ec.europa.eu/environment/water/water-framework/priority_substances.htm

[2] ISO Guide 34:2009 – General Requirements for the Competence of Reference Material Producers

10th International Conference on

Instrumental Methods of Analysis
Modern Trends and Applications

Heraklion, September 17-21, 2017

IMA-2017

www.ima2017.gr

Three Candidate Certified Reference Materials for Environmental Analysis

A. İsleyen[1], J. Vogl[2], D. Nikolic[3], A. Jotanovic[4], T. Näykki[5], N. Perkola[5], M. Horvat[6], A. Zoń[7], E. Bulska[8], M. Ochsenkuhn-Petropoulou[9], S. Zühtü Can[1], R. Jacimovic[6], L. Gažević[3], O. Cankur[1], B. Arı[1], M. Tunç[1], B. Binici[1], T. Gökçen[1], Z. Çakılbahçe[1], V. Lymberopoulou[9]

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[4]IMBIH- Institute of Metrology, Bosnia & Herzegovina
[5]SYKE-Finnish Environment Institute, Finland
[6]IJS-Institute Jozef Stefan, Slovenia
[7]GUM-Central Office of Measures, Poland
[8]UWAR-University of Warsaw, Poland
[9]NTUA-National Technical University of Athens, Greece

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Reliable analysis of chemical indicators in water and soil samples for the purpose of environmental pollution assessment poses one of the greatest analytical challenges, due to the complexity of sample matrix and low concentrations of pollutants. Organics (PFOS and PFOA) in ground water and heavy metals (Hg, Cd, Ni, Pb and As) in river water and soil represent main target parameters for the three candidate certified reference materials (CRMs). Laboratories performing sampling and tests in this field regulated by respective EU directives [1], need matrix CRMs enabling appropriate quality control. NMIs and DIs with proven metrological capabilities for the production and certification of such materials are necessary for the provision of quality data. Our project [2] is aiming to develop capacity to produce CRMs for environmental analysis by transferring the theoretical and practical know-how between the partners and combining their skills to focus on environmental CRM production according to ISO 17034 [3].

Raw materials were collected from locations in Turkey to ensure representation of the samples that laboratories are routinely analysing. River water was collected from a creek which is feeding a reservoir supplying water to İstanbul. Soil was collected from a coal burning power plant area at the district of Ankara. Ground water was collected from a well operating in İstanbul supplying water for the swimming pools and irrigation of gardens. After bottling, all CRM candidates were gamma sterilised to further enhance their stability and extend their shelf-lives.

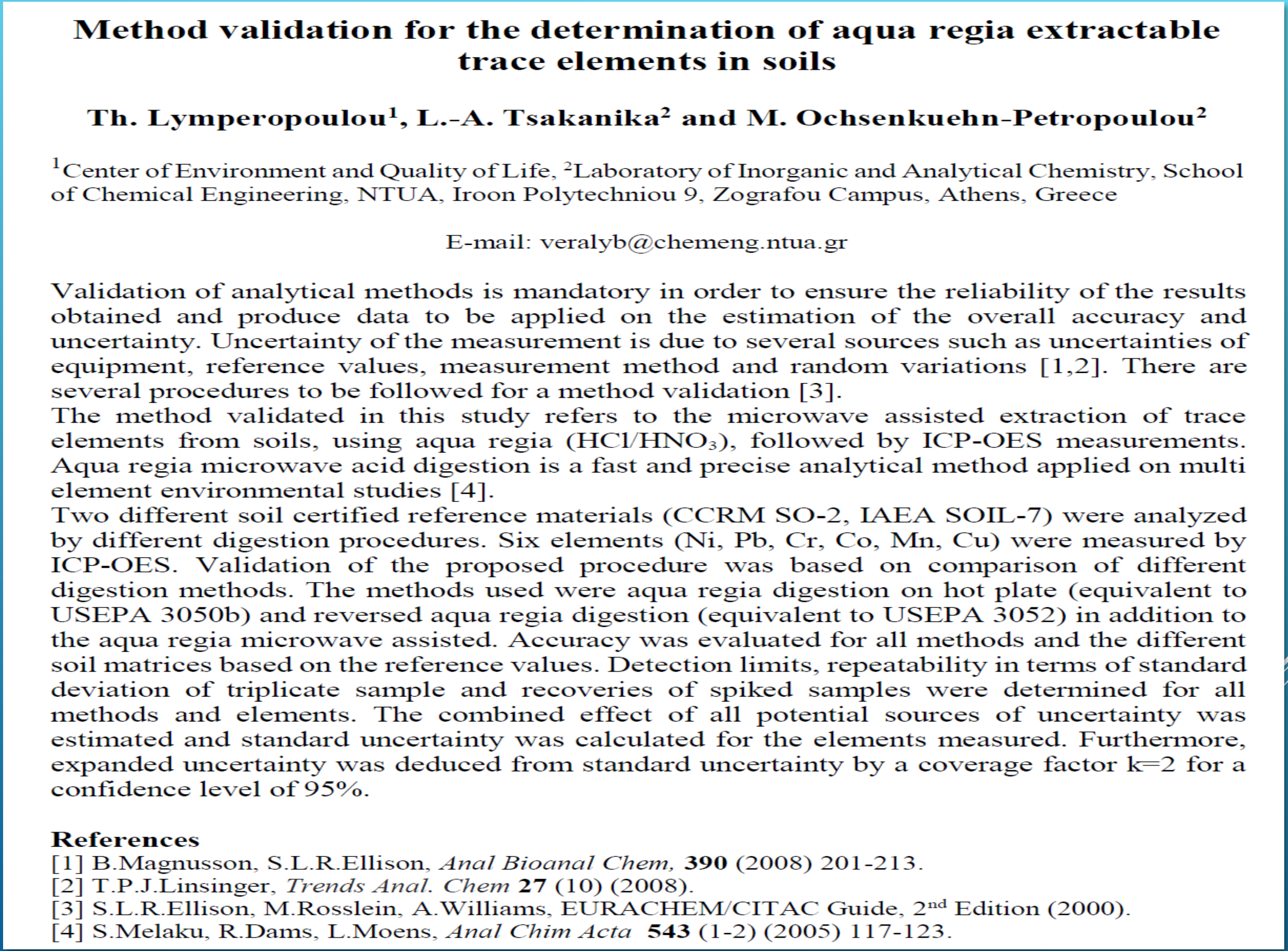
In this presentation, results of the homogeneity and stability tests will be shared with details of the material processing of candidate CRMs. Information about the characterization studies utilizing primary measurement techniques for the certification will also be presented.

References

[1] Water Framework Directive 2008/105/EC – Annex II: Priority substances and other pollutants http://ec.europa.eu/environment/water/water-framework/priority_substances.htm

[2] This project is funded by EMPIR which is co-funded by the EU's Horizon 2020 research and innovation programme and the EMPIR Participating States. For more information please visit http://www.envcrm.com

[3] International Organization for Standardization, ISO 17034, General requirements for the competence of reference material producers, ISO, Geneva (2015).



Method validation for the determination of aqua regia extractable trace elements in soils

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Validation of analytical methods is mandatory in order to ensure the reliability of the results obtained and produce data to be applied on the estimation of the overall accuracy and uncertainty. Uncertainty of the measurement is due to several sources such as uncertainties of equipment, reference values, measurement method and random variations [1,2]. There are several procedures to be followed for a method validation [3].

The method validated in this study refers to the microwave assisted extraction of trace elements from soils, using aqua regia (HCl/HNO_3), followed by ICP-OES measurements. Aqua regia microwave acid digestion is a fast and precise analytical method applied on multi element environmental studies [4].

Two different soil certified reference materials (CCRM SO-2, IAEA SOIL-7) were analyzed by different digestion procedures. Six elements (Ni, Pb, Cr, Co, Mn, Cu) were measured by ICP-OES. Validation of the proposed procedure was based on comparison of different digestion methods. The methods used were aqua regia digestion on hot plate (equivalent to USEPA 3050b) and reversed aqua regia digestion (equivalent to USEPA 3052) in addition to the aqua regia microwave assisted. Accuracy was evaluated for all methods and the different soil matrices based on the reference values. Detection limits, repeatability in terms of standard deviation of triplicate sample and recoveries of spiked samples were determined for all methods and elements. The combined effect of all potential sources of uncertainty was estimated and standard uncertainty was calculated for the elements measured. Furthermore, expanded uncertainty was deduced from standard uncertainty by a coverage factor k=2 for a confidence level of 95%.

References

[1] B.Magnusson, S.L.R.Ellison, *Anal Bioanal Chem,* **390** (2008) 201-213.
[2] T.P.J.Linsinger, *Trends Anal. Chem* **27** (10) (2008).
[3] S.L.R.Ellison, M.Rosslein, A.Williams, EURACHEM/CITAC Guide, 2nd Edition (2000).
[4] S.Melaku, R.Dams, L.Moens, *Anal Chim Acta* **543** (1-2) (2005) 117-123.

HEAVY METALS IN SOILS

- Heavy metals in soils occur naturally, by geological processes and anthropogenic activities
- For most analytical techniques sample digestion is required
- Numerous methods available resulting to total or partial decomposition depending on the sample matrix and involving mainly fusion or acid leaching

ACID EXTRACTION

- Acid-extraction or pseudo-total acid digestion methods have become a common procedure as an alternative to total digestion especially for laboratories that cannot or do not employ HF
- There is no consistent definition for acid leaching. It is considered as a wet procedure using different heating systems and a variety of mineral acids or their mixtures with molarities up to concentrated ones
- Acid extraction is ***operationally defined*** and does not necessarily release all elements completely

REFERENCE MATERIALS

- Reference materials characterized for both **acid extractable and total concentrations** of elements are of great value in environmental analytical chemistry especially when emphasizing on “environmental pollution” associated with anthropogenic activities

- Fractions of elements not released by aqua regia digestion are mostly bound to silicate minerals and are considered to lack environmental mobility

STANDARD METHODS FOR ACID EXTRACTION

- **ISO 11466.3:1995**
    - Aqua regia extraction – Hot plate digestion (open)
- **ISO 12914:2012**
    - Aqua regia extraction – Microwave digestion
- **USEPA 3052:1996**
    - Reversed aqua regia extraction – Microwave digestion

CERTIFIED REFERENCE MATERIAL BAM-U110 CONTAMINATED SOIL

(SANDY, SILICEOUS BY THE RIVER SAALE NEAR HALLE, DE)

	As	Pb	Cr	Cu	Mn	Ni	Co	Zn	Cd
	mg/kg								
U110 certified *Aqua regia extractable*	13.0	185	190	262	580	95.6	14.5	990	7.0
U110 measured	10.9	184	190	267	540	91.4	14.1	946	8.3
% accuracy	83.8	99.5	100.0	101.9	93.1	95.6	97.2	95.6	118.6
RSD %	1.8	2.3	4.0	8.5	2.3	2.2	1.0	9.1	0.2
Recovery % (spiked sample)	91	93	98	103	97	95	92	107	87
Detection limit µg/g	2.3	2.0	0.5	0.4	0.3	0.8	0.5	0.3	0.4

$$\%\ accuracy = \frac{measured\ value}{certified\ value} \times 100$$

SAMPLE TREATMENT

Reference Materials:
CCRM SO-2 (sandy, siliceous) and IAEA SOIL 7 (carbonaceous)

Method	reagent	vessel	heating	temperature, time
ISO 11466.3:1995	aqua regia ($HCl:HNO_3$ 3:1)	Pyrex beaker	hotplate	130 °C, 30 min
ISO 12914:2012	aqua regia ($HCl:HNO_3$ 3:1)	Teflon vessel	microwave apparatus*	180 °C, 15 min
USEPA 3052:1996	reversed aqua regia ($HCl:HNO_3$ 1:3)	Teflon vessel	microwave apparatus*	180 °C, 15 min

* START D, Milestone

ELEMENTS

		Ni	Pb	Cr	Mn	Cu	Co
LOD (µg/L)		1.6	4.4	7.8	0.8	1.5	1.3
LOQ (µg/L)		5.3	14.4	25.6	2.6	5.0	4.2
% Recovery (blank spiked)	**AR-HOT**	100.9	102.5	96.4	96.8	99.4	96.8
	AR-MW	104.5	99.4	102.2	99.3	97.3	104.2
	EPA	99.2	97.8	97.7	99.7	97.2	95.6

- (AR-HOT: ISO11466.3, AR-MW: ISO12914, EPA: USEPA3052)
- Determination of metals with a standard calibration method with ICP-OES Optima 7000 DV (Perkin Elmer) - wavelengths according to the ISO 11885:2009 (E), standard applied on water quality determination by ICP-OES

CCRM SOIL-2

Method	CCRM SO-2	Ni	Pb	Cr	Mn	Cu	Co
				mg/kg			
	reference values (total concentration)	8.0	21.0	16.0	720.0	7.0	9.0
AR-MW	values measured	4.9	16.0	10.5	413.6	7.1	9.4
	Uncertainty	0.6	1.9	1.2	48.6	0.8	1.1
	% repeatability	6.4	9.3	3.8	3.4	6.7	4.8
	% extractability	61.6	76.0	65.5	57.4	101.0	104.7
	% recovery (spiked sample)	97.3	99.4	98.8	99.3	97.3	99.4
EPA	values measured	4.5	16.6	9.2	383.6	7.5	6.1
	Uncertainty	0.5	1.9	1.1	45.0	0.9	0.7
	% repeatability	3.0	3.8	1.8	2.1	2.2	1.5
	% extractability	56.3	79.1	57.4	53.3	107.4	67.3
	% recovery (spiked sample)	96.8	96.5	99.0	99.7	104.6	95.6
AR-HOT	values measured	5.0	14.0	9.1	325.3	5.9	7.3
	Uncertainty	0.6	1.6	1.1	38.2	0.7	0.9
	% repeatability	4.6	9.1	5.1	6.1	3.3	4.4
	% extractability	62.4	66.4	57.2	45.2	83.9	81.1
	% recovery (spiked sample)	95.0	96.1	98.2	95.5	99.4	96.4

IAEA Soil 7

Method	IAEA SOIL 7	Ni	Pb	Cr	Mn	Cu	Co
		mg/kg					
	reference values (total concentration)	26.0	60.0	60.0	631.0	11.0	8.9
AR-MW	values measured	20.6	55.6	36.6	547.5	9.9	6.8
	Uncertainty	± 2.4	± 6.5	±4.3	±64.3	±1.2	±0.8
	% repeatability	6.4	9.3	3.8	3.4	6.7	4.8
	% extractability	79.2	92.7	61.0	86.8	90.2	75.9
	% recovery (spiked sample)	97.3	99.4	98.8	99.3	97.3	99.4
EPA	values measured	19.2	54.7	40.4	528.1	9.4	5.8
	Uncertainty	±2.3	±6.4	±4.7	±62.0	±1.1	±0.7
	% repeatability	3.0	3.8	1.8	2.1	2.2	1.5
	% extractability	74.0	91.2	67.4	83.7	85.6	64.8
	% recovery (spiked sample)	96.8	96.5	99.0	99.7	104.6	95.6
AR-HOT	values measured	17.8	49.0	32.6	541.0	8.7	6.3
	Uncertainty	±2.1	±5.8	±3.8	±63.5	±1.0	±0.7
	% repeatability	4.6	9.1	5.1	6.1	3.3	4.4
	% extractability	68.6	81.7	54.3	85.7	79.1	70.3
	% recovery (spiked sample)	95.0	96.1	98.2	95.5	99.4	96.4

MEASUREMENT UNCERTAINTY

$$u_{rel}(CON) = \sqrt{u_{rel}^2(C_A) + u_{rel}^2(V_{final}) + u_{rel}^2(m_{sample}) + u_{rel}^2(Rep)}$$

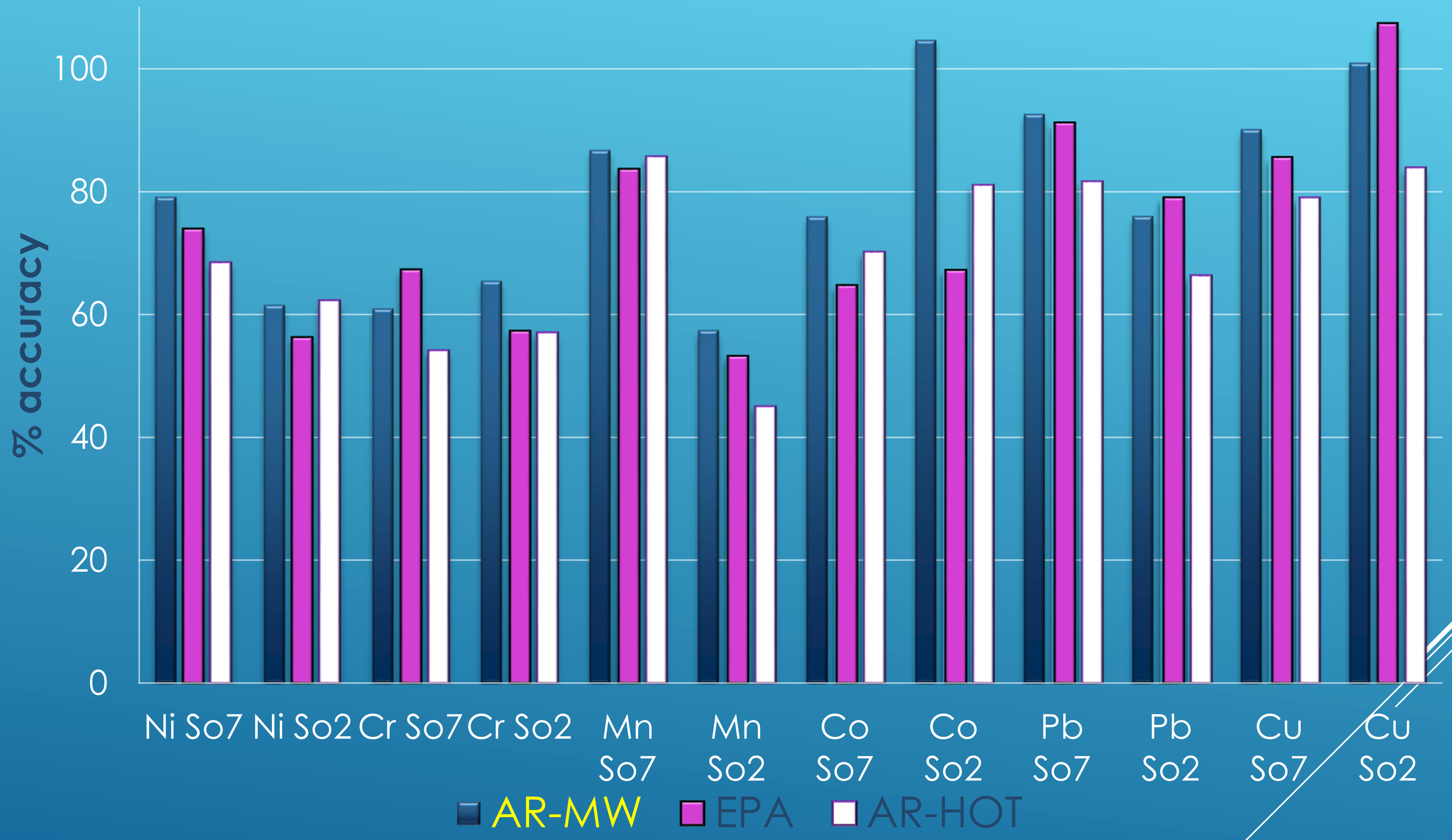
$u_{rel}(C_A)$: preparation of standard solution, repeatability
$u_{rel}(V_{final})$: dilution of the sample digest solution to the final volume of the digest
$u_{rel}(m_{sample})$: sample weight
$u_{rel}(Rep)$: relative standard deviation of measurements :Rep = RSD / SQRT (n)

temperature factor: $u_{vtemp} = \frac{3\,(V)(Q)}{1.73}$

Temperature Factor
the calculation of the uncertainty of standard solution $u_{rel}(C_A)$ and of the sample volume $u_{rel}(V_{final})$

(Qwater) = $2.1 \cdot 10^{-4}$ °C^{-1}
Expanded uncertainty (coverage factor k=2)

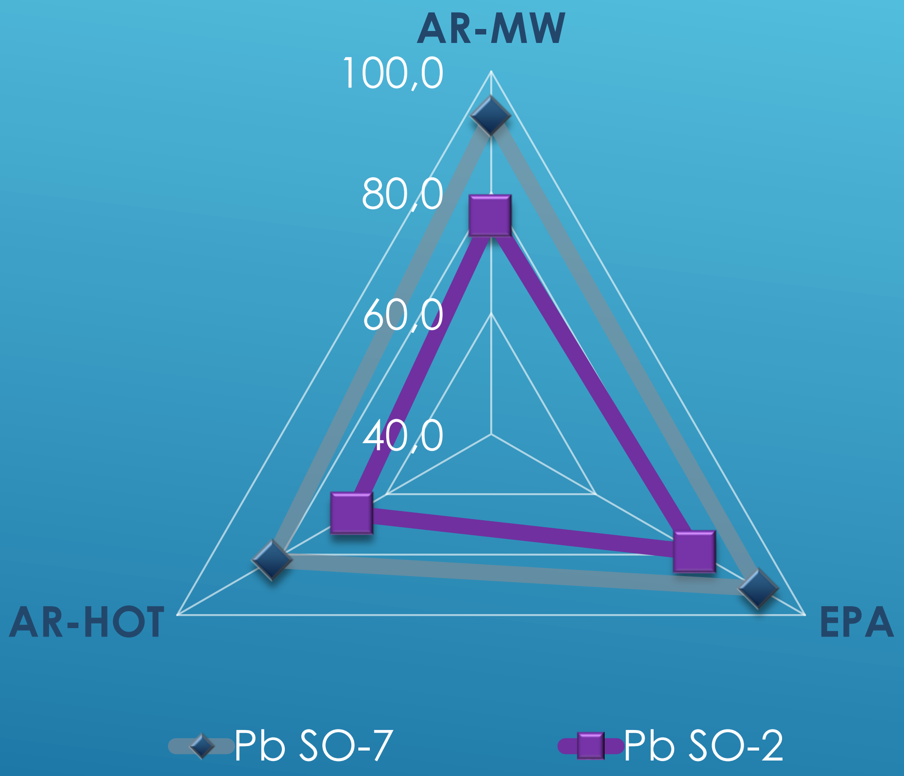
METHOD EXTRACTABILITY



So2: CCRM SO-2

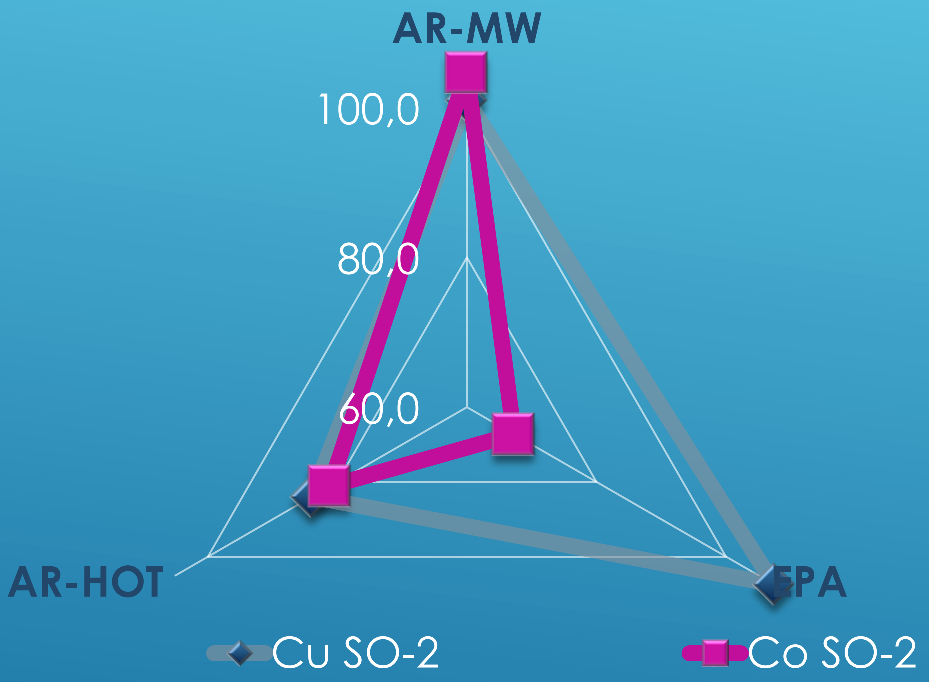
So7:IAEA SOIL 7

Lead extractability for different methods



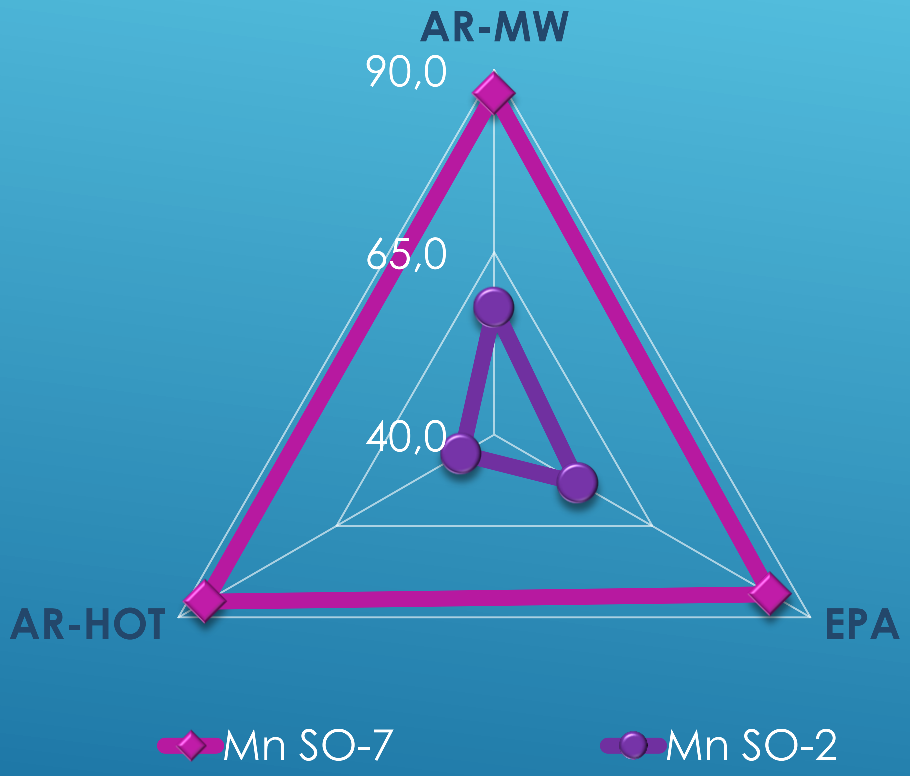
(AR-HOT: ISO11466.3, AR-MW: ISO12914, EPA: USEPA3052)

METHOD EXTRACTABILITY FOR DIFFERENT ELEMENTS



(AR-HOT: ISO11466.3, AR-MW: ISO12914, EPA: USEPA3052)

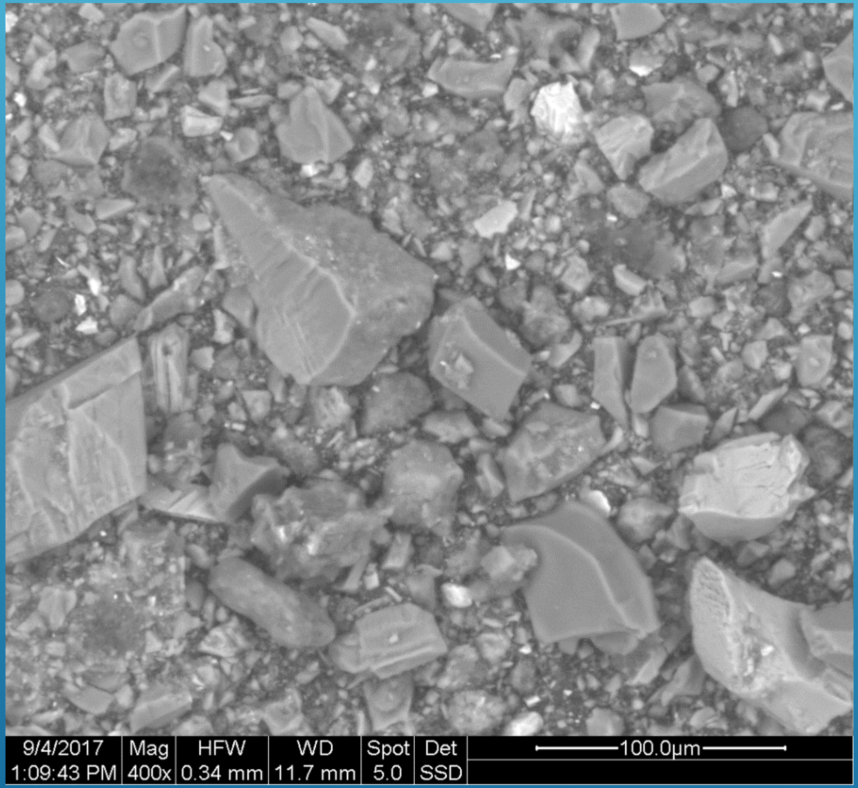
MANGANESE EXTRACTABILITY FOR DIFFERENT MATRICES



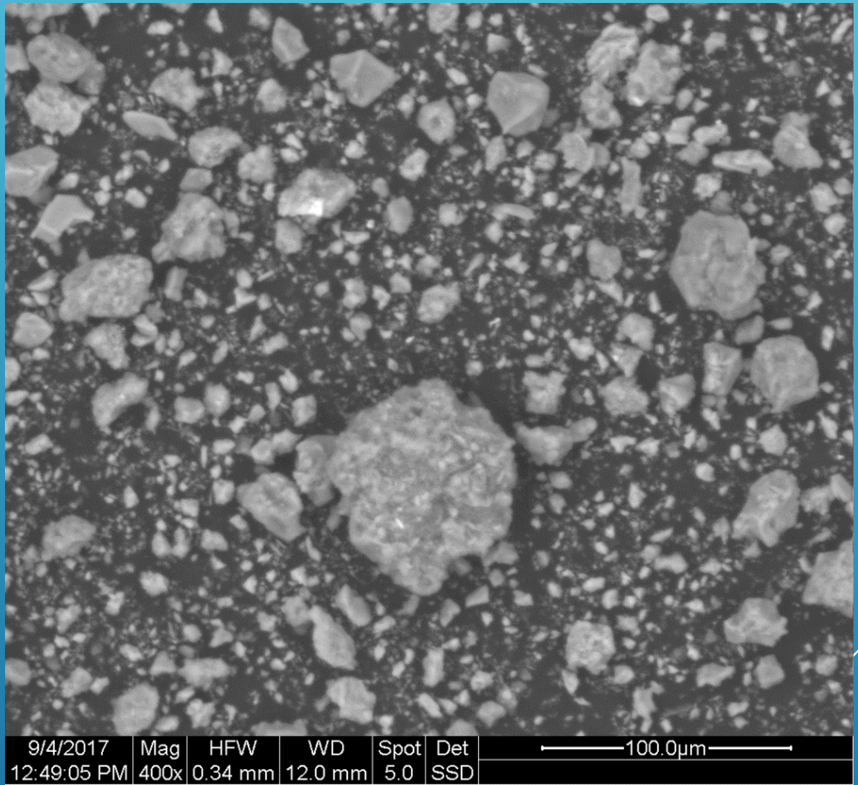
(AR-HOT: ISO11466.3, AR-MW: ISO12914, EPA: USEPA30)

MORPHOLOGY-PHASE DISTRIBUTION

CCRM SO-2



IAEA SOIL 7



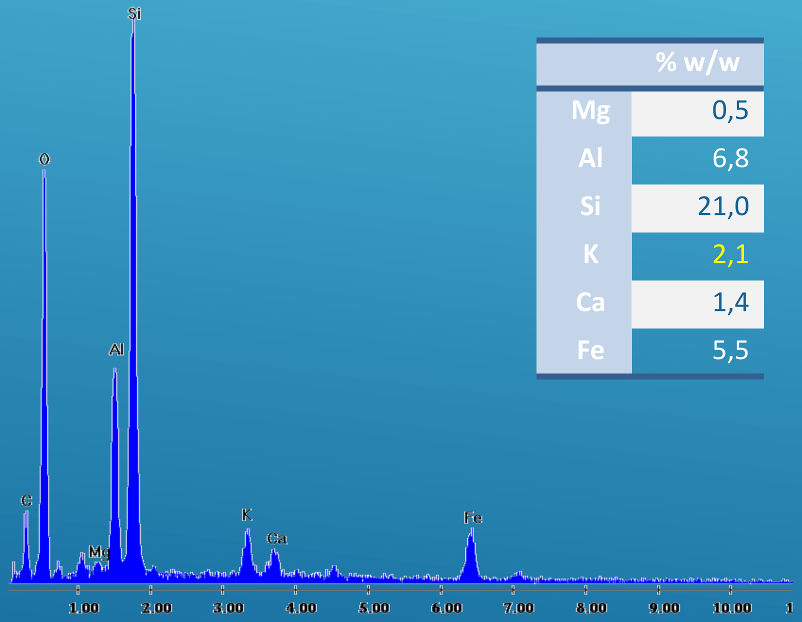
Fei 200 Quanta SEM/EDAX

ELEMENTAL-MINERALOGICAL COMPOSITION

CCRM SO-2

sandy, siliceous

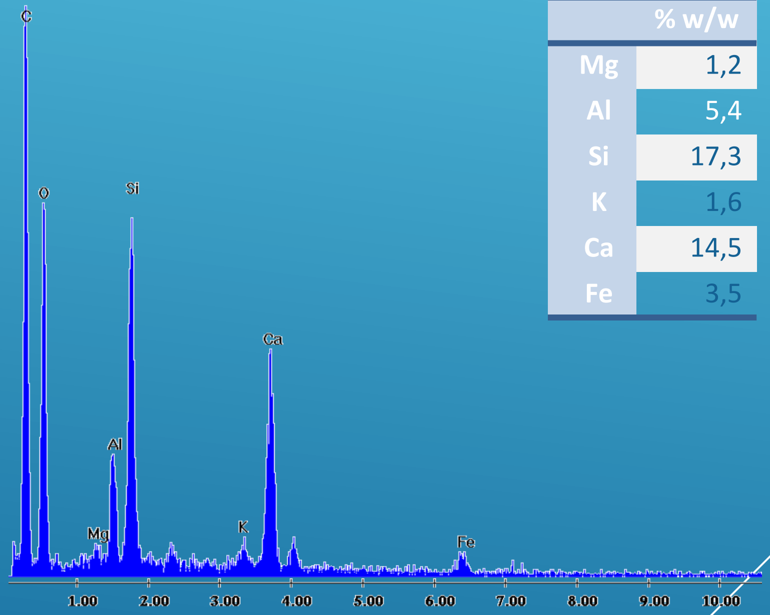
	% w/w
Mg	0,5
Al	6,8
Si	21,0
K	2,1
Ca	1,4
Fe	5,5



IAEA SOIL 7

carbonaceous

	% w/w
Mg	1,2
Al	5,4
Si	17,3
K	1,6
Ca	14,5
Fe	3,5



Fei 200 Quanta SEM/EDAX

TUBITAK CANDIDATE REFERENCE MATERIALS

Method: ISO 12914:2012			
aqua regia (HCl:HNO_3 3:1)	Teflon vessel	Microwave apparatus	180 °C, 15 min

CONCLUSIONS

- ✓ Levels of elements determined after **aqua regia procedure** should not be considered as "total values"- a fraction of element may remain in the residue.
- ✓ **ISO 12914:2012** is considered as optimum for soils with low organic content.
- ✓ The accuracy (extraction capability) of all methods depends on the type of sample and the determined element . The efficiency of extraction might differ from element to element and also for the same element in different matrices.
- ✓ The main component of method uncertainty is the **relative standard deviation** of measurements

Thank you for your attention

EnvCRM

EMPIR

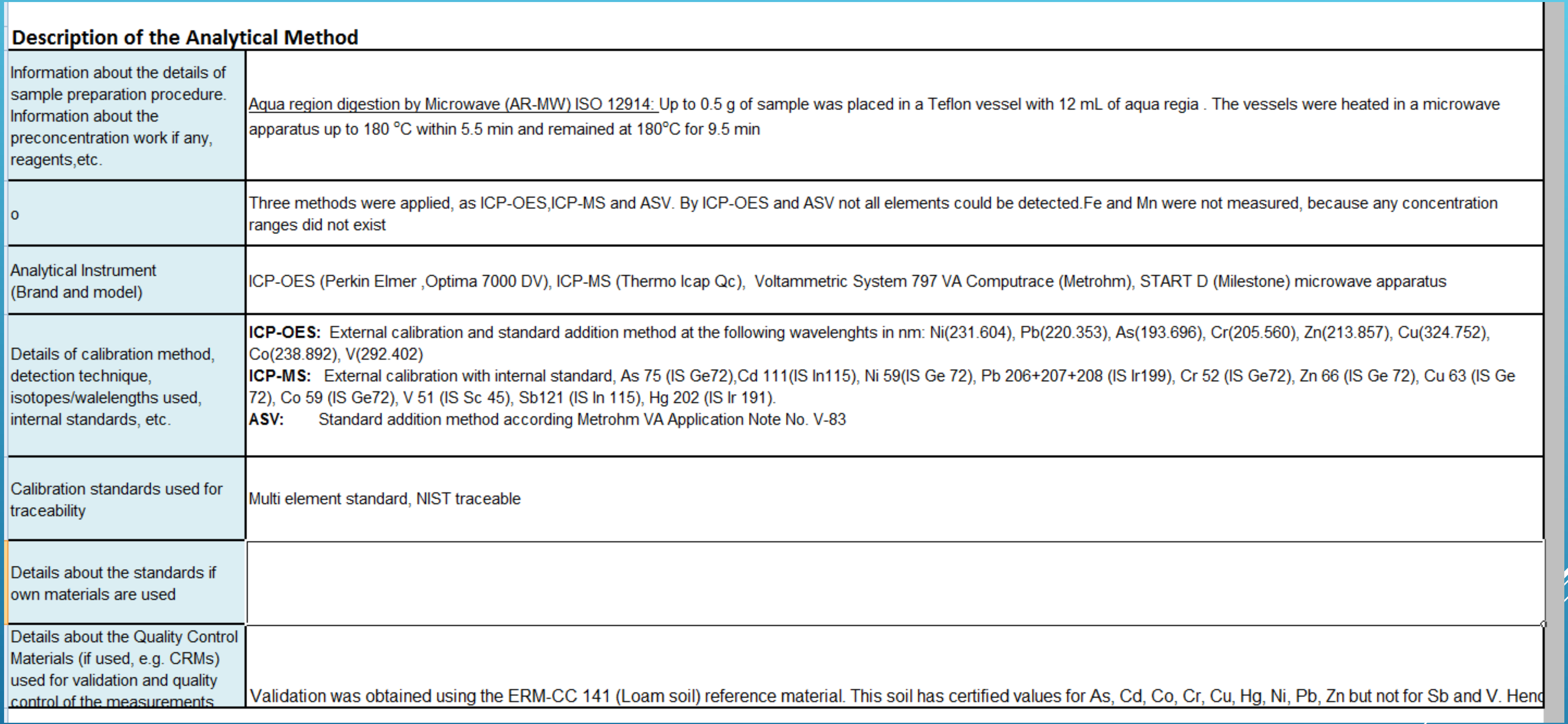
EURAMET

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

ENVCRM: Matrix Reference Materials for Environmental Analysis
WORKSHOP ON REFERENCE MATERIALS,
TUBITAK UME , Gebze Turkey , 16/05/2018

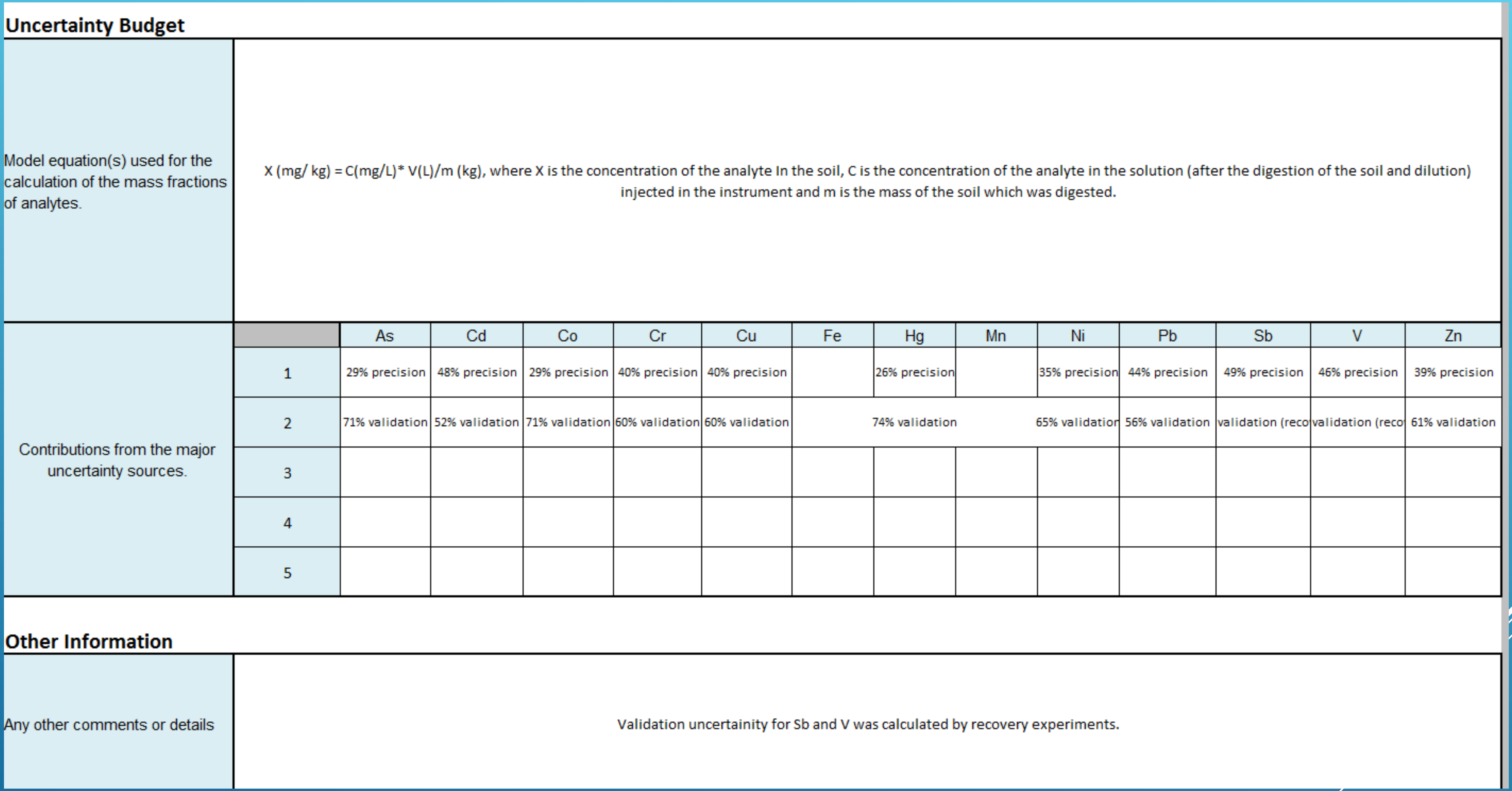
MEASUREMENTS RESULTS

Bottle No.	Run No.	Sample mass	Mass fractions (mg/kg)												
		(g)	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sb	V	Zn
47	1 (ICP-OES) cal	0.5	59±3.1	n.d.	42±1.1	55±3.3	81±5.6	–	n.d.	–	48±2.3	61±2.7	n.d.	57±1.9	127±3.9
	2 (ICP-OES) stadd	0.5	68±3.6	n.d.	44±1.1	62±3.7	79±5.4	–	n.d.	–	57±2.7	71±3.2	n.d.	70±2.3	132±4.1
	3 (ICP-MS) cal+IS	0.5	69±3.7	1.19±0.038	40±1.0	68±4.1	61±5.2	–	0.3±0.009	–	49±2.3	62±2.8	1.53±0.054	67±2.2	130±4.0
	4 (ASV) stadd	0.5	n.d	1.35±0.24	n.d	n.d	71±2.1	–	n.d.	–	n.d.	72±7.1	n.d.	n.d.	131±9.2
1101	1 (ICP-OES) cal	0.5	62±3.3	n.d.	42±1.1	55±3.3	75±5.1	–	n.d.	–	47±2.2	61±2.7	n.d.	58±1.9	136±4.2
	2 (ICP-OES) stadd	0.5	71±3.8	n.d.	46±1.2	62±3.7	72±4.9	–	n.d.	–	57±2.7	69±3.1	n.d.	69±2.3	139±4.3
	3 (ICP-MS) cal+IS	0.5	69±3.7	1.2±0.038	41±1.0	69±4.1	61±4.2	–	0.3±0.009	–	49±2.3	63±2.8	1.55±0.055	68±2.2	130±4.0
	4 (ASV) stadd	0.5	n.d	1.14±0.26	n.d	n.d	73±2.9	–	n.d.	–	n.d.	71±7.4	n.d.	n.d.	133±9.2
Mean			66.3*	1.22*	42.5*	61.8*	72*	–	0.3*	–	51.2*	66.3*	1.54*	64.8*	132.3*
Standard Deviation			4,7	0,09	2,2	6	7,4				4,6	4,9	0,01	5,8	3,8
Combined standard uncertainty (u_c)			9%	9%	4%	6%	7%		11%		6%	6%	2% (*)	3% (*)	4%
Coverage factor (k)			2	2	2	2	2		2		2	2	2	2	2
Expanded uncertainty (U)			17%	18%	9%	12%	14%		22%		11%	11%	5% (*)	5% (*)	9%
* The mean values refer to the average of the results obtained for the different instrument (method) used and for three replicates. For this purpose				by the three methods used for three replicates each.				The standard deviation refer to these mean values.							



Description of the Analytical Method

Information about the details of sample preparation procedure. Information about the preconcentration work if any, reagents,etc.	Aqua region digestion by Microwave (AR-MW) ISO 12914: Up to 0.5 g of sample was placed in a Teflon vessel with 12 mL of aqua regia . The vessels were heated in a microwave apparatus up to 180 °C within 5.5 min and remained at 180°C for 9.5 min
o	Three methods were applied, as ICP-OES,ICP-MS and ASV. By ICP-OES and ASV not all elements could be detected.Fe and Mn were not measured, because any concentration ranges did not exist
Analytical Instrument (Brand and model)	ICP-OES (Perkin Elmer ,Optima 7000 DV), ICP-MS (Thermo Icap Qc), Voltammetric System 797 VA Computrace (Metrohm), START D (Milestone) microwave apparatus
Details of calibration method, detection technique, isotopes/walelengths used, internal standards, etc.	**ICP-OES:** External calibration and standard addition method at the following wavelenghts in nm: Ni(231.604), Pb(220.353), As(193.696), Cr(205.560), Zn(213.857), Cu(324.752), Co(238.892), V(292.402) **ICP-MS:** External calibration with internal standard, As 75 (IS Ge72),Cd 111(IS In115), Ni 59(IS Ge 72), Pb 206+207+208 (IS Ir199), Cr 52 (IS Ge72), Zn 66 (IS Ge 72), Cu 63 (IS Ge 72), Co 59 (IS Ge72), V 51 (IS Sc 45), Sb121 (IS In 115), Hg 202 (IS Ir 191). **ASV:** Standard addition method according Metrohm VA Application Note No. V-83
Calibration standards used for traceability	Multi element standard, NIST traceable
Details about the standards if own materials are used	
Details about the Quality Control Materials (if used, e.g. CRMs) used for validation and quality control of the measurements	Validation was obtained using the ERM-CC 141 (Loam soil) reference material. This soil has certified values for As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Zn but not for Sb and V. Hend



Uncertainty Budget

Model equation(s) used for the calculation of the mass fractions of analytes.	X (mg/ kg) = C(mg/L)* V(L)/m (kg), where X is the concentration of the analyte In the soil, C is the concentration of the analyte in the solution (after the digestion of the soil and dilution) injected in the instrument and m is the mass of the soil which was digested.

		As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sb	V	Zn
Contributions from the major uncertainty sources.	1	29% precision	48% precision	29% precision	40% precision	40% precision		26% precision		35% precision	44% precision	49% precision	46% precision	39% precision
	2	71% validation	52% validation	71% validation	60% validation	60% validation		74% validation		65% validatio	56% validation	validation (reco	validation (reco	61% validation
	3													
	4													
	5													

Other Information

Any other comments or details	Validation uncertainity for Sb and V was calculated by recovery experiments.

Measurement uncertainty

$$\frac{U(x)}{[x]} = \sqrt{\left(\frac{U_{bias}}{[x]_{CRM}}\right)^2 + RSD^2 + \left(\frac{U(m)}{m}\right)^2 + \left(\frac{U(V)}{V}\right)^2 + \left(\frac{U(c)}{c}\right)^2}$$

Validation (CRM or recovery experiments)

Precision

Measurement of mass

Measurement of volume

Calibration

Expanded uncertainty (coverage factor k=2)