Publishable Summary for 20IND01 MetroCycleEU
Metrology for the recycling of Technology Critical Elements to support Europe's circular economy agenda

Overview

Technology critical elements (TCE) are key materials for high-level technology but their supply to the EU is challenging. A sustainable solution to this problem is through recovery and recycling, but the analysis of waste streams is difficult and a complicating factor. The overall objective of this project is to enable the representative SI traceable determination of TCE at the µg/g level in urban mine wastes. Transferable calibration methods and appropriate reference material(s) are being developed to improve TCE analysis for recycling in the context of the circular economy. Targeted industries in the recycling chain include multinational companies, SMEs and R&D institutes.

Need

TCE are a group of naturally occurring chemical elements increasingly used in high technology, including energy-efficient lighting, electric car batteries, sensors, electronic devices, mobile phones and computers, due to their unique characteristics (conductivity, magnetism, material properties). These elements are considered 'critical' because of their economic importance in essential technologies and their supply risk (stock depletion and/or few producers in, for example, Russia, China and Africa). In addition, only relying on raw materials as the prime source for TCE has an environmental cost due to the industrial mining required to supply the scarce raw materials. Because of the shift towards a greener economy through the deployment of renewable energy and e-mobility solutions (European Green Deal), the demand for TCE is expected to increase exponentially in Europe. The value of raw materials in electronic waste generated in Europe in 2019 alone was estimated to be approximately 12.9 billon USD. The need to secure TCE supply has become even more pressing under the current health crisis and invasion of Ukraine by Russia. It is therefore a major objective of the EU's Covid-19 Recovery Plan and the REPowerEU action aimed at reinforcing Europe's resilience and autonomy.

In order to secure the TCE supply, the EU has promoted more efficient recycling and waste collection through the amended Waste Framework Directive (2018/851/EU). At the same time, the Circular Economy Action Plan has set a target of 50 % reduction in municipal waste disposal by 2030 and there are plans for various European legislation (on batteries, packaging, end-of-life vehicle and electronic equipment....) to be reviewed to stimulate better management of TCE-containing wastes, to increase the recycled content, and ensure high-quality recycling. In 2020, the EU established a list of the critical elements for Europe. The TCE included in the MetroCycleEU project (Cobalt (Co), Gallium (Ga), Germanium (Ge), Indium (In), Tantalum (Ta), Neodymium (Nd), Praseodymium (Pr), Dysprosium (Dy), Gadolinium (Gd), Lanthanum (La), Gold (Au), Platinum (Pt), Palladium (Pd), Rhodium (Rh) and Lithium (Li)) were selected from this list.

Wastes from the urban mine are extremely heterogeneous, which makes the estimation of their TCE content difficult. Currently there is a lack of knowledge at the European level about the TCE stocks and flows in the urban mine. Given the high volume of waste generated and received, fast reliable preparation and analytical methods as well as sampling and sample preparation strategies are needed to determine the economic value of the waste and of the final product, to decide on recycling route and to engage in new R&D for recycling. Prior to this project a survey was circulated by NMIs to identify the metrological needs of industries involved in urban mine waste recycling. This survey highlighted the lack of reference materials certified for TCE in these wastes and the need for specific validated methods and documentary standards for TCE to comply with ISO/IEC 17025 requirements.

Objectives

The overall objective of the project is to provide reliable and SI traceable determination of TCE in urban waste material at µg/g levels in order to increase the efficiency and accuracy of TCE recycling.

The specific objectives of the project are:

1. To develop validated SI-traceable reference methods (e.g. ICP-MS, INAA) to determine mass fractions at µg/g levels in urban waste materials with a target combined uncertainty below 10 % for the TCEs Co, Ga, Ge, In, Ta, Nd, Pr, Dy, Gd, La, Au, Pt, Pd, Rh and Li. In addition, sampling and digestion strategies for the reference methods will be optimised specifically for TCE in urban waste matrices.

2. To develop traceable and validated reference materials for the TCE in Objective 1 and to use them to validate TCE mass fraction measurements in urban mine waste with a target combined uncertainty below 20 %.

3. To validate the use of the methods and reference materials from objective 1 and 2 using inter-laboratory comparisons involving at least 10 industrial laboratories using both destructive methods (e.g. ICP-MS, ICP-OES) and non-destructive or quasi non-destructive analysis (e.g. WD-XRF, GD-OES, LIBS).

4. To facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain, standards developing organisations (i.e. those associated with the Waste Framework Directive (2018/851/EU) and ISO/IEC 17025 and end users (recycling industry, analytical laboratories).

Progress beyond the state of the art

Urban mine wastes are highly complex and heterogeneous materials, which require suitable processing, sampling and digestion prior to analysis. Reaching complete dissolution of the materials is highly challenging and several digestion protocols have been tested and their individual performances are being compared. In parallel, the recovery obtained with easier and safer protocols (leaching protocols) are being tested as alternative solution that are more adequate for routine analysis. At the same time, two methods are being developed that do not require sample dissolution: neutron activation (INAA) and laser ablation (LA-ICP-MS). As expected, INAA is a very powerful tool to determine TCE concentration in the solids. The feasibility has been demonstrated for LA-ICP-MS quantification of TCE and will be validated by comparison with ICP-MS and INAA analysis.

There is a lack of information about the most suitable combination of reference methods for analysis of TCE in waste materials and the most appropriate processing and digestion techniques. Due to the large heterogeneity of the matrix compositions of the urban mine waste, no harmonised sampling or sample preparation protocols exist. After reviewing the literature and initial testing, a sampling plan including several steps of size reduction and sub-sampling has been applied to printed circuit boards, ending with 27 final subsamples. The 27 subsamples were analysed by ICP-MS for TCE and the uncertainty factor were calculated. Results show that TCE behave differently during the milling step; while some TCE such as Nd are most affected by the first milling step at 30-10mm, the heterogeneity for other TCE such as Co is mostly attributed to the final miling step at 200 µm.

Currently no suitable reference material exists for TCEs in urban mine wastes thus preventing method validation in compliance with quality standards (ISO/IEC 17025) and adequate calibration/optimisation of instruments, such as XRF spectrometry. Three candidate materials are currently being evaluated: printed circuit board (PCB), Li-ion Batteries (LiB) and LED. One of the main challenge was to develop the best size reduction strategy, which is different for all three materials The most challenging to reduce in powder were PCB and LED as they contain metal scraps. For PCB the best method was chosen but the resulting material was not identical to the initial batch material. At least one of these materials will be certified for TCEs with an expanded uncertainty below 20 %.

The reference methods developed in the project are relevant for the certification of reference materials but require specific capabilities that are too expensive and time-consuming for routine use. This project will improve the calibration and use of XRF instruments specifically for TCE analysis in urban waste materials. Furthermore, methods will be developed to enable the use of the materials characterised within the project as calibrants or quality controls to improve accuracy. An interlaboratory comparison involving laboratories beyond the consortium will be organised to validate the use of these methods and the reference material developed within the project.

Results

Reference TCE analysis methods, sampling and sample preparation for the selected TCEs in urban mine waste (Objective 1)

The project is developing and optimising reference methods for the sample preparation and TCE analysis of three urban mine wastes: Printed Circuit Boards (PCB), LED and Li-ion batteries (LiB). These three materials have been sourced in sufficient quantities for the project.

For method development, a test batch of PCB was crushed and different digestion strategies (alkali fusion, microwave assisted acid digestion, plasma ashing) were assessed by ICP-MS analysis. All elements are being recovered at near 100% yields with alkali fusion after ashing. Regarding acid digestion, however, some elements (e.g Ta) require the addition of hydrofluoric acid to dissolve completely. In parallel, interferences correction instrumentation (HR-ICP-MS, ICP-MS/MS, ICP-CC-MS) have been optimised and compared. Results show that in this PCB, all 14 TCE are present, but Pt and Rh content are below the target of 1 mg/kg. Given the difficulty of reaching the complete digestion of the material, digestion protocols for partial dissolution of the material but resulting in full or near-total recovery of the TCE are being tested. These complete recovery methods will be compared with a simpler, safer approach with a mixture of nitric and hydrochloric acid, which may be sufficient to reach 80% recovery. To validate this strategy, techniques of analysis that do not involve dissolution are being optimised. Powdered PCB material was pelletized and subsequently analysed by LA-ICP-MS. The obtained signal appeared rather heterogeneous, therefore efforts were focused on data processing to smoothen the signal. Following data processing, RSDs of <10% could be obtained for most elements measured, with the rest falling below 20%. In conclusion, this technique could be a viable option for direct measurement of PCB material. The method developed will be validated by comparison with ICP-MS analysis. Non-destructive instrumental neutron activation analysis (INAA) of the crushed PCB and LED samples has been carried out and matrix interferences were determined. The approach successfully achieved combined relative uncertainties at percent level for Au, La, Co and Ta, while only detection limits were reached for Ga, In and Nd. However, the INAA data were in good agreement with the preliminary results from ICP-MS.

A second PCB sample, issued from a 400 kg batch has been prepared. After a review of the sampling protocols available, a sampling and preparation plan has been decided consisting of 3 steps of subsampling and size reduction down to 27 tests portion (~0.5g) at a grain size of 200-500 µm. The 27 subsamples were analysed by ICP-MS for TCE and the uncertainty factor were calculated. Results show that TCE behave differently during the milling steps; while some TCE such as Nd are most affected by the first milling step at 30-10mm, the heterogeneity for other TCE such as Co is mostly attributed to the final miling step at 200 µm. A part of the samples prepared under this sampling plan will be used for the preparation of the project reference material.

For LED, (initial batch size of 17kg) the crushing method has been optimised but with significant difficulties encountered. For this material, a 4-step process was required to obtain a <200 µm powder, but further developments are necessary to crush the amount required for the production of a reference material. Results from ICP-MS analysis show that the TCE present >1 mg/kg are Co, Ga, In, Ta, Nd, Dy, Gd, La, Au, Pt, and Li.

For LiB, a portion of the initial sample (~50g) was successfully crushed to below 200 µm thanks to the acquisition of a new equipment and it is now being analysed by ICP-MS. The crushing of the whole batch (5kg) is nearly complete.

Urban mine waste reference material for the determination of mass fractions of TCEs (Objective 2)

A certification strategy has been agreed between the partners for the candidate reference materials to permit production and certification according to ISO 17034 General requirements for the competence of reference material producers. The optimised crushing processes assessed within objective 1 will be reused to produce the final material for homogeneity and stability tests as well as material characterisation for the certification.

Improvement of industrial routine analysis (Objective 3)

From an industrial perspective, XRF spectrometry is commonly used as a rapid approach to identify and potentially quantify the chemical composition of solid wastes. However, the performance and accuracy of such instruments is not known for the TCE analysis in waste materials. In the course of the project, the reference material and the method developed will help improve the calibration of XRF instruments for the determination of TCE content in wastes. Most TCE from the project cannot be quantified with satisfying recovery with XRF, except for Co. Therefore, XRF is mainly focused on a limited list of elements that are actually detectable and present within the PCB (e.g. Co, Ba, Ni). A survey has gathered useful information to further understand the needs of the industry. Results of the survey show that the most interest is on the lithium battery and then the printed circuit board.

Impact

The project has been presented at 18 European and 2 national conferences dedicated to analytical chemistry and/or material recycling.

Impact on industrial and other user communities

The industrial end-users who will benefit from the project are: 1) industries that recycle and analyse TCE, 2) industries and organisations that collect and trade wastes (which are usually different from recycling companies), 3) accredited analytical laboratories (recycling industry sub-contractors) and laboratories from R&D public institutes involved in waste recycling, 4) TCE analysis instruments manufacturers (e.g. XRF) and material providers. These end-users will be able to improve and validate their measurement methods for TCE analysis in their premises, improve the quality and accuracy of their data, calculate the uncertainties and improve their sampling strategies through the use of the reference material, the interlaboratory comparison (ILC), technical guides, videos and calculation tools available. As a result, these end users will gain robust knowledge of the commercial values of their wastes to decide on a recycling route. In the longer term, regulatory bodies and policy makers will benefit from the increased quality and quantity of data to take actions to promote TCE waste recycling.

One partner of the project is a member of the newly created (2020) European Raw Materials Alliance, a network of stakeholders, including industrial actors along the value chain, Member States and regions, trade unions, civil society, research and technology organisations, investors and NGOs. This will facilitate the dissemination of the outcome of MetrocycleEU.

Impact on the metrology and scientific communities

Most of the project partners are active members in working groups and technical committees of the Inorganic Analysis Working Group (IAWG) of the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) of the BIPM and EURAMET. Both organisations encourage the progress beyond the state of the art in chemical measurement science. Activities carried out within the project will provide supporting evidence on National Metrology Institutes' (NMIs') ability to perform TCE concentration measurements in complex matrices.

The metrological infrastructure will help the organisers of proficiency testing and large-scale reference material producers to use matrix matched reference materials in order to guarantee the quality of the TCE measurements under ISO/IEC 17025 accreditation.

Impact on relevant standards

The project will support the implementation of the Circular Economy Action Plan from the European Green Deal, through the development of methods for TCE analysis in recyclable wastes from the urban mine. In addition, the consortium will promote the results of the project within the standardisation community and will provide input to the standardisation process (ISO, CEN). The reference measurement procedures developed will also be disseminated to NMIs and relevant designated institutes (DIs) through participation in meetings and workshops organised on behalf of CCQM.

Longer-term economic, social and environmental impacts

With the expected increase in TCE recycling and demand, the economic value of the wastes should rise and the need for more high-quality data will increase. In 2019, in Europe, the amount of urban mine waste generated from electrical and electronic equipment (WEEE) was estimated to be around 12 million tonnes and the value of raw materials in this electronic waste approached 12.9 billon USD. The loss of TCE to waste is therefore also an economic loss and makes recycling a more pressing matter, as well as resilience to raw material crises and international market fluctuations. This project will support the implementation of various Directives such as the WEEE Directive (2012/19/EU), Waste Framework Directive (2018/851/EU), Batteries and Accumulators Directive (2006/66/EC), End-of-Life Vehicle Directive (2000/53/EC) and the Eco-design Directive (2009/125/EC). By making available best practice guides for routine analysis, more laboratories will be able to implement TCE measurements satisfying quality standards at lower cost.

Securing the TCE supply also affects the life of European citizens, as TCE are essential to provide the necessary digital products and services (e.g. smartphones, sensors) in addition to critical industries such as the medical sector, the transportation sector, industry, power plants etc. and even to sectors that were traditionally not “connected” such as agriculture.

List of publications

1. MICHALISZYN, Lena, PRAMANN, Axel, RÖTHKE, Anita, *et al.* Combining standard addition and isotope dilution in order to improve SI traceable LA-ICP-MS measurements. *Journal of Analytical Atomic Spectrometry*, 2022, vol. 37, no 11, p. 2442-2450. *https://doi.org/10.1039/d2ja00243d*
2. DI LUZIO, Marco et D’AGOSTINO, Giancarlo. The k0-INRIM software version 2.0: presentation and an analysis vademecum. *Journal of Radioanalytical and Nuclear Chemistry*, 2022, p. 1-10.*https://doi.org/10.1007/s10967-022-08622-5*
3. Trimmel, S., Meisel, T.C., Lancaster, S.T. et al. Determination of 48 elements in 7 plant CRMs by ICP-MS/MS with a focus on technology-critical elements. Anal Bioanal Chem (2023). https://doi.org/10.1007/s00216-022-04497-3
4. Klein, O., Zimmermann, T., Ebeling, A. et al. Occurrence and Temporal Variation of Technology-Critical Elements in North Sea Sediments—A Determination of Preliminary Reference Values. Arch Environ Contam Toxicol 82, 481–492 (2022). https://doi.org/10.1007/s00244-022-00929-4
5. LANCASTER, Shaun T., PROHASKA, Thomas, et IRRGEHER, Johanna. Low-level ^{40}Ca determinations using nitrous oxide with reaction cell inductively coupled plasma–tandem mass spectrometry. *Analytical and Bioanalytical Chemistry*, 2022, p. 1-8.*https://doi.org/10.1007/s00216-022-04146-9*
6. LANCASTER, Shaun T., PROHASKA, Thomas, et IRRGEHER, Johanna. Characterisation of gas cell reactions for 70+ elements using N 2 O for ICP tandem mass spectrometry measurements. *Journal of analytical atomic spectrometry*, 2023, vol. 38, no 5, p. 1135-1145. https://doi.org/10.1039/D3JA00025G

This list is also available here: https://www.euramet.org/repository/research-publications-repository-link/

Project start date and duration:	01 June 2021, 36 months	
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Internal Funded Partners: 1. LNE, France 2. BAM, Germany 3. IMBiH, Bosnia and Herzegovina 4. INRIM, Italy 5. LGC, United Kingdom 6. PTB, Germany 7. RISE, Sweden 8. SYKE, Finland 9. TUBITAK, Turkey	External Funded Partners: 10. BRGM, France 11. EID, France 12. Hereon, Germany 13. MUL, Austria	Unfunded Partners: 14. JSI, Slovenia 15. METAS, Switzerland
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