



Germanium speciation study in soil from an electronic waste processing plant area

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Abstract

Purpose Germanium (Ge) is known as a Technology Critical Element (TCE) and has been widely used in electronic and industrial products. Waste electronic and electrical equipment (WEEE) containing germanium goes to WEEE treatment plants. The transfer of Ge in the environment makes it necessary to get to know its mobility, reactivity, and chemical transformations in soil. The objective of this research was to develop a methodology for germanium speciation in soil under pressure from storage, processing, and recovery from electrowaste.

Materials and methods Thirty soil cores (30 cm long) were collected from an area around a WEEE plant, using a Humax soil sampler. Soil magnetometry methods were used for the first time during the determination of soil sampling points for germanium. After basic physicochemical analysis (pH, Eh, total element concentration using the ICP-MS technique), soil samples were prepared for germanium speciation. The optimisation and validation of a methodology for determining Ge species in easily-leached fractions of soil collected from areas around an electrowaste plant, was studied using Ion Chromatography-Inductively Coupled Plasma-Mass Spectrometry (IC-ICP-MS). Chromatographic conditions were optimised, taking soil matrix effects into account. Optimised Ge extraction from the soil included: extraction time, type of extractants, extraction support using shaking, and ultrasound.

Results and discussion The Ge species (Ge(IV), monomethylgermanium (MMGe), and dimethylgermanium (DMGe)) were successfully separated after 12 min on a Dionex IonPac AS9-HC column with ammonium nitrate and potassium sodium tartrate as an elution phase. The highest extraction efficiency was achieved by using 100 mM NH_4NO_3 with 1 mM potassium sodium tartrate as an extractant, that washes out Ge from soils within 4 h. In most cases, the soils contained a Ge(IV) form. Germanium methyl derivatives were only found in a few soil samples. Our research showed that germanium concentration in the studied area was as high as $7.64 \text{ mg}\cdot\text{kg}^{-1}$, with an average concentration of $3.51 \text{ mg}\cdot\text{kg}^{-1}$. The results allowed the creation of a correlation matrix, which identified many strong correlations.

Conclusion This research confirmed the impact of a WEEE plant on the increase of the Ge content in topsoil, when in direct proximity. Increased germanium content occurred in soil samples located north of the emitter, which is consistent with the prevailing wind direction. The study confirmed that the soil magnetometry method is applicable for detecting TCE. Soil samples with the highest content of germanium had a very high magnetic susceptibility and there is a correlation between these parameters.

Keywords Ge(IV) · Methyl germanium species · IC-ICP-MS · Soil pollution · Toxic elements speciation · Electrowaste

1 Introduction

Germanium is recognised as a critical and rare element (Yellishetty et al. 2017), while its properties are exploited in electronics and renewable energy applications on an

increasingly large scale. An increase in Ge use has been observed in new technologies. For this reason, the risk of its uncontrolled release into the soil is growing through the disposal of waste electrical and electronic equipment (WEEE) (Işıldar et al. 2018; Julander et al. 2014). Industrial interest in this element raises the need to assess its potential environmental impact (Perkins et al. 2014). Germanium is one of the Technology Critical Elements (TCE) (Jabłońska-Czapla and Grygoyć 2022; Jabłońska-Czapla et al. 2022; Wojcieszek

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et al. 2017) and has been widely used in electronic and industrial products like semiconductor detectors, the optical and telecommunication industries, wind turbines, electric vehicles, photovoltaics, and energy-efficient lighting (Nuss and Blengini 2018). The increasing use of modern technologies leads to the release of more and more quantities of TCE into the natural environment. For this reason, the scientific community is increasingly interested in the natural processes associated with TCEs, as well as their impact on living organisms and their potential threat to human health (Cobelo-García et al. 2015). Germanium dioxide intake is known to cause serious side effects, including organ dysfunction and even death. The global mean concentration of Ge in topsoil is estimated at $2 \text{ mg}\cdot\text{kg}^{-1}$ and varies in the range $< 0.1\text{--}15.0 \text{ mg}\cdot\text{kg}^{-1}$, when considering the variety of soils forming under strongly different pedogenic conditions (Wiche et al. 2018). The global concentration of germanium in soil depends on geogenic and anthropogenic factors. For example, a study of the mining area of Freiberg (Germany) showed that the total concentration of Ge in soil varied considerably, ranging from $1.0\text{--}4.3 \text{ mg}\cdot\text{kg}^{-1}$ (mean $1.9 \text{ mg}\cdot\text{kg}^{-1}$) (Wiche et al. 2017).

The main analytical techniques for determining the total germanium content in soils are atomic spectrometric techniques, such as Inductively Coupled Plasma Optical Emission Spectroscopy ICP-OES (Rosenberg 2007), Inductively Coupled Plasma Mass Spectrometry ICP-MS (Delvigne et al. 2017; Okoroafor et al. 2022), Atomic Absorption Spectroscopy AAS (Hambrick et al. 1984), High Resolution Inductively Coupled Plasma Mass Spectrometry HR-ICP-MS (Delvigne et al. 2009), Laser Ablation Inductively Coupled Plasma Mass Spectrometry LA-ICP-MS (Belissont et al. 2014), and spectrophotometry (Soylak and Yigit 2015).

The metal and metalloid species in which they occur have a significant impact on their mobility, reactivity, transformation, and toxicity (Templeton and Fujishiro 2017). Therefore, speciation analysis is very important to understanding its natural behaviour in nature or determining the toxicity and ecotoxicity (Krystek and Ritsema 2004; Tricas et al. 2014). Germanium occurs as Ge(II), Ge(IV), Monomethylgermanium (MMGe), dimethylgermanium (DMGe), and Trimethylgermanium (TMGe). Germanium methyl derivatives are produced by methylation, assisted by microorganisms (Rosenberg 2009; Thayer 2002). In seawater, methylated forms of germanium account for 70% of dissolved germanium (Romero-Freire et al. 2019). However, there is insufficient information in the literature on the content of methyl derivatives of this element in soils. It was found that Ge(IV) displays nutrient-like behaviour in estuaries and surface waters, similar to silicon (Padro et al. 1995). Hyphenated techniques are useful for analysing different germanium forms (Lehmann et al. 2019; Padro et al. 1995). Ge species may be separated by liquid chromatography, often with the addition of chelating agents for complexation (Smichowski

and Marrero 1998). In ICP-MS techniques, the application of a dynamic reaction cell (DRC) allows for the elimination of mass spectral interference (Zhang et al. 2017). Little is known about the geochemical behaviour and speciation of Ge in soils (Wiche et al. 2018). Ge speciation in soil solutions and its mobility in soils may strongly depend on the pH. Acidic soil conditions and a high proportion of germanium in the organic fraction may affect the availability of this element to plants (Wiche and Heilmeyer 2016).

The content of germanium in soils, around the areas associated with the processing of electronic waste has not yet been widely studied. The only studies on trace metal content from e-waste (electrowaste)-contaminated soils were carried out by Cui et al. (2017). However, they only tested the content of metals such as Cd, Pb, Zn, Cr, Ni, and Cu. Our earlier study (Jabłońska-Czapla et al. 2021) showed that the highest concentration of germanium was found in the topsoil, and it was over $8 \text{ mg}\cdot\text{kg}^{-1}$. The mean concentration of germanium in the upper soil layer was $4.8 \text{ mg}\cdot\text{kg}^{-1}$. The concentration of this element fell as the soil profile increased in thickness, with few exceptions; the lowest concentration of germanium occurred in the soil samples with a thickness of 15–18 cm of the soil profile. Therefore, one of the objectives of the research was to identify which species of germanium occur in areas near to WEEE processing plants. The second aim was the optimisation and validation of a methodology for determining the matrix effects and extracting the inorganic Ge(IV) and methylated derivatives (monomethylgermanium (MMGe) and dimethylgermanium (DMGe)) from easily-leached soil fractions using Ion Chromatography-Inductively Coupled Plasma-Mass Spectrometry (IC-ICP-MS).

2 Materials and methods

2.1 Sampling area and sample preparation

Samples were collected around the WEEE (Waste Electrical and Electronic Equipment) plant located in the Metropolis of Upper Silesia and Zagłębie in Poland (Fig. 1). This area is the most industrialised and heavily urbanised area of Poland, where numerous enterprises related to the mining and metallurgical industries are located. The company itself is located in the southern, densely forested district of Katowice City and collects used devices and components from electrical and electronic devices. The company is also interested in any waste containing precious metals such as gold, silver, palladium, platinum, rhodium, and iridium. The germanium content in the waste stored and processed in the plant was confirmed in our previous studies (Fornalczyk et al. 2019; Willner et al. 2021). Wastes are segregated and collected according to type, and stored in containers and large bags on a hard surface. The storage site is covered, which protects

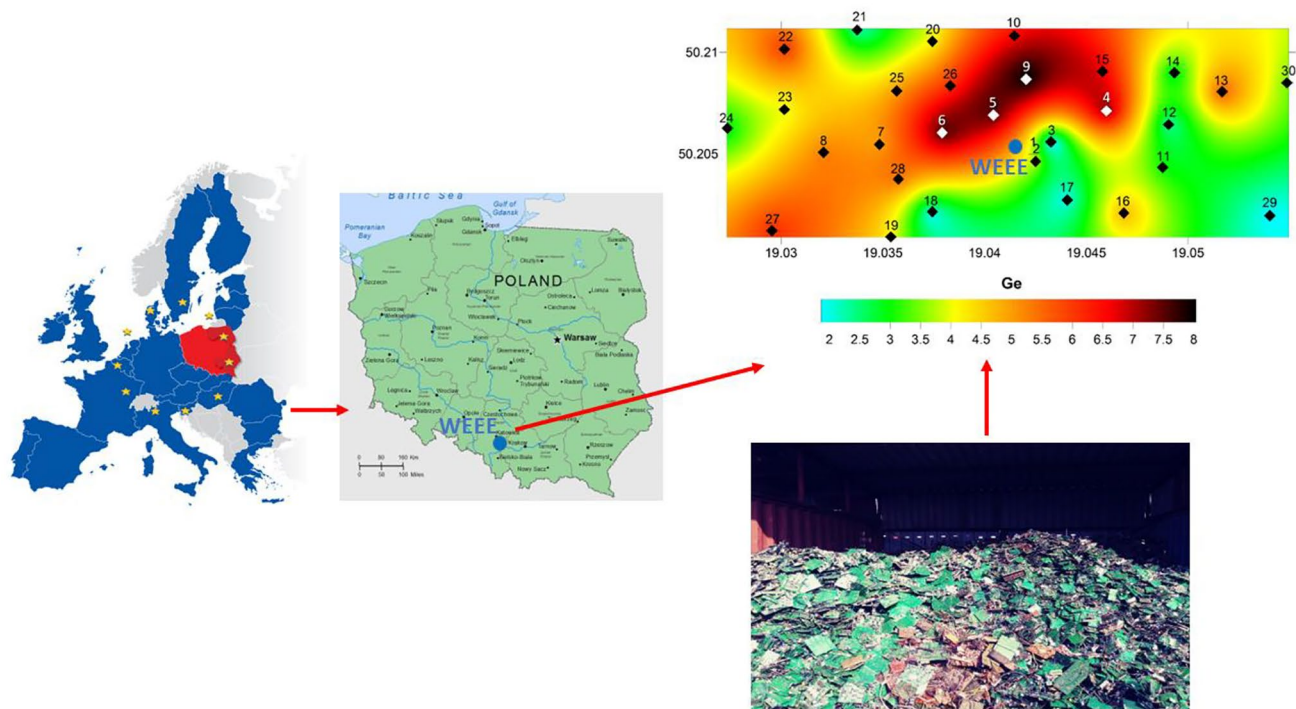


Fig. 1 Sampling area and spatial distribution of the sampling points and total germanium content in soil samples from the area surrounding the WEEE processing plant

the waste from contact with rainfall and prevents the leakage of metal compounds and hazardous substances directly into the soil. In one of the closed halls, the manual disassembly of electronic elements and components is carried out. In another closed hall, the process of ‘skinning’ copper cables is performed with the use of a cable recycling machine. In addition, soil samples were collected in an agricultural area near Lublin (Poland), which was not subjected to industrial anthropopressure, and treated as background readings.

In the beginning, the low-field volume magnetic susceptibility (κ) was measured *in situ* using an MS2 Bartington meter, equipped with an MS2D loop sensor. Sixty points of surface magnetic susceptibility measurements were performed on the study area. At each point, the κ value (expressed in 10^{-5} SI units) was calculated as the mean value of 11 readings within 2m^2 . The localisation of individual sampling points was confirmed using a Garmin GPS navigation device. Soil samples were collected in a similar way to previous studies (Rachwał et al. 2015, 2017a, b). From 30 selected sampling points, two 30 cm long soil cores were collected using a Humax soil sampler. Immediately after sampling, the soil cores were placed in tubes to limit contact with atmospheric air and ore impurities. On the same day that the samples were taken, they were delivered to the institute's laboratory. After transporting soil cores to the laboratory, to determine the vertical distribution of magnetic susceptibility and (indirectly) the depth of migration

of pollutants along the soil cores, the magnetic susceptibility was measured using a Bartington MS2C meter with a resolution of 1 cm. From the depths characterised by the highest values of magnetic susceptibility (generally 3–6 cm), the soil samples were separated and subjected to chemical analysis after air drying, averaging, and sieving through a sieve with a diameter of 2 mm. Air dried samples were stored in polypropylene (PP) containers and analysed within one month.

The basic physicochemical parameters of soils, such as pH and Eh (redox potential), were determined the day after the samples were delivered to the laboratory. Redox potential was measured using an ERPt-111 electrode (Elmetron, Zabrze, Poland) and pH was measured using an ERH-111 electrode (Elmetron, Poland).

2.2 Reagents and standards

Standard solutions for total germanium determination were prepared from a $1000\text{mg}\cdot\text{L}^{-1}$ germanium standard for ICP and $100\text{mg}\cdot\text{L}^{-1}$ metalloid non-metal mix for ICP, both from Sigma-Aldrich (Switzerland). The certified ICP-MS quality control standard no.1, ICP-MS calibration standard no. 2, and ICP-MS Multi-element standard solution VI (AccuStandard, USA) were used for other elements in the total analysis of the matrix. All working solutions were prepared with acidified (suprapur 65% nitric acid, Merck, Darmstadt, Germany), deionized water obtained from an ultrapure

Hydrolab water purification system (HLP 10 UV, Poland). An internal standard $10 \mu\text{g L}^{-1}$ rhodium (Merck, Darmstadt, Germany) solution was used. Standard stock solutions for the HPLC speciation of germanium species (DMGe, MMGe and Ge(IV)) were prepared from dimethyldichlorogermane ($\text{CH}_2\text{Cl}_2\text{Ge}$, 99%, Acros Organics, UK), methyltrichlorogermane ($\text{CH}_3\text{Cl}_3\text{Ge}$, 97%, Gelest, USA) and germanium(IV) oxide (GeO_2 , 99.9%, Aldrich Chemistry, USA). The mobile phase was prepared by dissolving an appropriate amount of ammonium nitrate ($\geq 99.0\%$, Sigma-Aldrich, USA) and potassium sodium tartrate tetrahydrate (99%, Sigma-Aldrich, USA). In addition, diluted phosphoric acid (85%, Merck) was used to improve elution strength.

2.3 Determination of the total content of germanium

The soil core samples were transported to the laboratory and preliminary operations were performed, consisting of air-drying, manual grinding in a porcelain mortar and sieving through a sieve with a 2 mm diameter mesh. This procedure allowed for separation into so-called earthy and skeletal parts. The last step was to grind samples in an electric mortar and sieving to a < 0.2 mm grain diameter.

Soil samples were digested in acidic conditions (2 ml HNO_3 , 6 ml HCl and 3 ml HF) in an Anton Paar 3000 (Austria) microwave oven. A 0.2 g air-dried soil sample was transferred to a vessel and digested at 1400 W power for 30 min. After digestion, the solution was poured into a polypropylene volumetric flask and diluted to 50 ml. The 73324 Certified Reference Material of soil (China National Analysis Center for Tron and Steel, Beijing, China) was used for quality control in the analysis of total germanium.

To carry out soil sampling with maximal signal intensity and minimal interference effects during the analysis, the instrument parameters, such as quartz torch position, voltages of ionic lenses, radio frequency detector power, nebuliser gas flow, and DRC reaction gas flow, were optimised. The final working conditions are listed in Table 1.

The total content of Ge and other elements in the matrix were determined using an Elan 6100 DRC-e ICP-MS spectrometer (PerkinElmer, USA). Samples and standards were delivered with a peristaltic pump. The spectrometer was optimised daily, with a $10\text{-}\mu\text{g L}^{-1}$ solution (Mg, Cu, Rh, Cd, In, Ba, Ce, Pb, and U) in 1% HNO_3 Elan 6100 Setup/Stab./Masscal. Solution (PerkinElmer). The concentrations of metals were measured with the internal ^{103}Rh standard.

Germanium determination using ICP-MS spectroscopy is difficult because of numerous spectral interferences: ^{70}Ge ($^{35}\text{Cl}^{17}\text{O}^{18}\text{O}^+$, $^{36}\text{Ar}^{34}\text{S}^+$, $^{38}\text{Ar}^{32}\text{S}^+$, $^{70}\text{Zn}^+$), ^{72}Ge ($^{36}\text{Ar}_2^+$, $^{56}\text{Fe}^{16}\text{O}^+$, $^{40}\text{Ar}^{32}\text{S}^+$, $^{40}\text{Ar}^{16}\text{O}_2^+$, $^{55}\text{Mn}^{16}\text{OH}^+$), and ^{74}Ge ($^{40}\text{Ar}^{34}\text{S}^+$, $^{36}\text{Ar}^{38}\text{Ar}^+$, $^{40}\text{Ar}^{36}\text{S}^+$, $^{37}\text{Cl}_2^+$, $^{74}\text{Se}^+$) (Filella and

Table 1 Optimised working conditions of the ICP-MS Elan 6100 DRC-e spectrometer

Parameter	Value
ICP-MS	
RF power [W]	1125
Plasma gas flow [L/min]	15
Nebulizer gas flow [L/min]	0.76–0.82
Auxiliary gas flow [L/min]	1.15–1.16
Nebulizer type	Cross flow
Plasma torch	Quartz
Scanning mode	Peak hopping
Dwell time [ms]	100
Sweeps/reading	20
Number of replicates	3
Rpq value	0.65
CH_4 flow [mL/min]	0.4

Rodushkin 2018; Zhang et al. 2017). In order to eliminate these polyatomic interferences, DRC technology (with CH_4 as the reaction gas) was used. The flow rate of the reaction gas and the value of the rejection parameter (Rpq) were the key parameters of the DRC operation. The optimised CH_4 flow rate was selected at 0.4 mL min^{-1} and when the Rpq value was 0.65, the signal of ^{74}Ge tended to be stable. Under the optimised conditions, the analytical performance of the proposed method was evaluated. Standard solutions with Ge concentrations from 1 to $25 \mu\text{g L}^{-1}$ were analysed to construct a calibration curve with a correlation coefficient of 0.9998.

2.4 Method development of germanium speciation

Three germanium species were simultaneously separated and determined by HPLC, combined with an ICP-MS spectrometer. The technical characteristics of the equipment were: a high-performance liquid chromatograph Series 200 (Perkin Elmer) system including a Peltier column oven, autosampler, gradient pump, vacuum degasser, and control unit. An anion exchange IonPac AS9-HC (Dionex) column ($250 \text{ mm} \times 4 \text{ mm}$, $9 \mu\text{m}$) was chosen to successfully separate the $\text{Ge}(\text{OH})_4$, DMGe, and MMGe forms. The samples and standard solutions were injected via a $200 \mu\text{l}$ sample loop on a column. HPLC kit was hyphenated with an ICP-MS DRC-e Elan 6100 (Perkin Elmer) spectrometer as an elemental detector via a valve and Scotch-type spray chamber. The determination of Ge was conducted using the ICP-MS technique in DRC-e mode, to remove polyatomic plasma- and matrix-based interferences. The optimised working conditions of the ICP-MS instrument are presented in Table 1.

Samples were extracted for soil speciation analysis. Liquid extraction is not as efficient as microwave digestion; however, high temperatures and reagents may change the degree of oxidation of element species. The method of soil extraction was optimised to extract as much germanium as possible. 10 ml of 100 mM potassium sodium tartrate was added to 2 g of the sample. Extraction was carried out using an ultrasonic cleaner (Sonic 5, Polsonic, Warszawa, Poland), and then the samples were centrifuged by a Beckman Coulter Avanti JXN-26 centrifuge (20,000 rpm, JA-25.50 Fixed-Angle Aluminium Rotor type).

The optimisation of germanium extraction from soils was conducted using various solutions: 20 mM Na₂EDTA; 100 mM citric acid with 20 mM Na₂EDTA pH 3.8; 100 mM citric acid; 300 mM ammonium tartrate; 100 mM NH₄NO₃ with 1 mM potassium sodium tartrate; and 100 mM potassium sodium tartrate. Extraction efficiency, using the optimised method, was calculated as the ratio of germanium species determined by HPLC-ICP-MS to total germanium determined by ICP-MS, after microwave digestion.

The solution was then subjected to HPLC-ICP-MS analysis. Germanium compounds were separated by employing a gradient of a mixture of 7 mM NH₄NO₃, 1 mM potassium sodium tartrate tetrahydrate (pH 5) (adjusted by adding HNO₃), 100 mM NH₄NO₃, 1 mM potassium sodium tartrate, and 20 mM H₃PO₄ (pH 2.1). Potassium sodium tartrate had to be added to each sample, up to a final concentration of 80 mM to each sample and standard solution, to avoid co-elution of germanium forms. The total time for separating germanium forms was 12 min. The optimised separation parameters for the simultaneous determination of DMGe, MMGe, and inorganic Ge(IV) species are presented in Table 2.

2.5 Method validation of germanium speciation

The calibration curve was obtained by measuring the calibration standard solutions of germanium species five

times. A 1 g·L⁻¹ stock standard solution of DMGe, MMGe, and Ge(OH)₄ were mixed before analysis, to reach final concentrations of 0.5, 1.0, 2.5, 5.0, 7.5, and 10.0 µg·L⁻¹ of each form, subjected to the extraction procedure and analysed by the HPLC-ICP-MS system. The average intensity value for each standard was taken to construct the calibration curve. Example chromatograms, obtained during the calibration of the IC-ICP-MS system, are shown in Fig. 2a.

An 80 mM potassium tartrate solution was used to prepare all blanks, standards, and sample dilutions. The respective correlation coefficients obtained were: 0.9996, 0.9999, and 0.9997 for DMGe, MMGe and Ge(IV). A linear model of the dependence of the concentration of the total number of analyte counts was selected. The chosen operating ranges for calibration curves were statistically verified by checking the distribution of variances using Snedecor's F test. The limit of detection (LOD) and quantification was calculated from mixed standard solution calibration curves and was based on the following dependencies (1):

$$LOD = \frac{3.3SD}{b} \quad (1)$$

where LOD is the limit of detection; SD is a standard deviation value; and b is the slope of the calibration curve. The limit of quantification was set as three times the LOD.

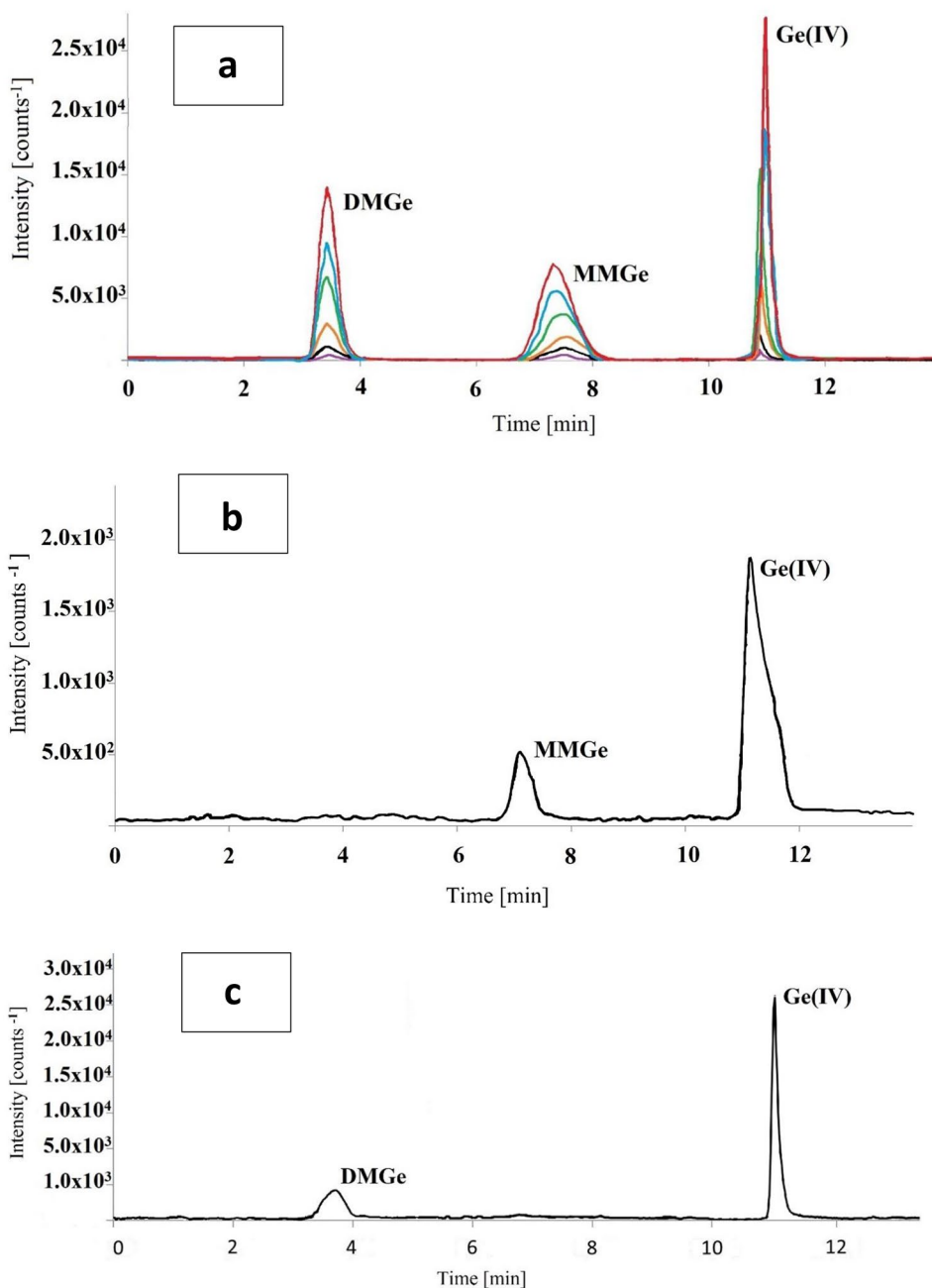
The standard deviation values were determined as the standard deviation of 10 replicates of mixed standard solutions at concentrations of 0.5, 5.0, and 10.0 µg·L⁻¹ and subjected to the extraction procedure for DMGe, MMGe, and Ge(IV), respectively. Repeatability was evaluated for germanium forms in real samples after five replicate analyses. The recovery was determined with measurements of the real samples spiked with a known amount of mixed standard solution containing all investigated species. The selected method validation parameters are presented in Table 3.

Matrix effect (ME) refers to the matrix, which often significantly interferes with the analyte analysis process. It is an

Table 2 Optimised separation parameters for simultaneous determination of DMGe, MMGe and inorganic Ge(IV) species

Parameter	Value
Separation column	Dionex IonPack™ As9-HC (4 × 250 mm, 5 µm)
Temperature	25 °C
Mobile phase	A: 7 mM NH ₄ NO ₃ , 1 mM KNaC ₄ H ₄ O ₆ ·4H ₂ O, pH = 5 (HNO ₃) B: 100 mM NH ₄ NO ₃ , 1 mM KNaC ₄ H ₄ O ₆ ·4H ₂ O, 20 mM H ₃ PO ₄ , pH = 2.1
Elution program	0–4.5 min 100% A; 4.5–10 min 100% B; 10–12 min 100% A
Flow rate	0.8 mL min ⁻¹
Retention time of Ge species [min]	DMGe 3.41 min MMGe 7.46 min Ge(IV) 10.96 min
Volume of sample	100 µL

Fig. 2 **a** Superimposed chromatograms obtained after analysing standard solutions of MMGe, DMGe, and Ge(IV) with concentrations of 0.5, 1.0, 2.5, 5.0, 7.5, and 10.0 $\mu\text{g}\cdot\text{L}^{-1}$, respectively; **b** chromatogram of the real soil sample No. 5 taken from the area surrounding the WEEE processing plant; **c** chromatogram of the real soil sample No. 4 taken from the area surrounding the WEEE processing plant



important parameter that affects the selectivity and sensitivity of the quantitative analysis and is calculated using Eq. (2):

$$ME(\%) = \left(\frac{k_1}{k_2} - 1 \right) \times 100\% \quad (2)$$

where ME(%) is the matrix effect; k_1 is the slope of the matrix standard curve; and k_2 is the slope of the solvent standard.

When the value of ME(%) is > 50%, there is a strong matrix effect. If the value is between 20–50%, there is a medium matrix effect. No matrix effect is considered when

ME is in the range 0–20%. Positive and negative values mean signal enhancement or suppression induced by the matrix, respectively (Yang et al. 2021).

To determine Ge species accurately, matrix effects were evaluated by performing standard addition calibrations and external calibrations (D'Amore et al. 2023). The MEs calculated using Eq. (2) were between –20% and 20%, indicating that there was no matrix effect. In addition, the values of spike recovery were tested by F-tests. At a confidence level of 95%, no significant differences were found.

Table 3 Validation parameters for the simultaneous determination of germanium species

Parameter	Value		
	DMGe	MMGe	Ge(IV)
Linear Equation	$y = 9828x + 240$	$y = 10510x - 905$	$y = 11120x + 1048$
R ²	0.9996	0.9999	0.9997
Limit of Quantification, $\mu\text{g kg}^{-1}$	0.9	1.1	0.8
Limit of Detection, $\mu\text{g kg}^{-1}$	0.3	0.4	0.3
Recovery, %	98	97	102
Uncertainty, %	15.0	17.6	11.3

3 Results and discussion

3.1 Optimisation of the chromatographic separation

Our research included the chemical speciation of germanium, directly determined by chromatographic separation (HPLC) followed by elemental detection ICP-MS. In this study, we developed the method described in Lehmann et al. (2019). However, some modifications were necessary. This was because the above-mentioned authors conducted their research using an instrument with much better analytical performance, equipped with a triple quadrupole. In this work, we used an instrument with a single quadrupole and a different collision/reaction cell gas. Therefore, it was necessary to make some improvements to the method, to be able to carry out the study. Optimisation of the mobile phase composition was conducted to achieve the best possible separation of DMGe, MMGe, and inorganic Ge signal. The method was optimised by different conditions, such as injection volume, the concentration of tartrate in the sample and gradient pump flow. To improve the separation, different amounts of potassium sodium tartrate were added to the standards and the effect was checked. With an 80 mM concentration of tartrate, separation was not fully successful because DMGe and MMGe forms were not separated. Increasing the tartrate concentration to 100 mM resulted in good resolution and sharp peak shapes. The addition of potassium sodium tartrate to samples and standards is necessary to avoid the co-elution of three Ge species. Germanium species forms were separated by employing a gradient of a mixture of: 7 mM NH_4NO_3 , 1 mM potassium sodium tartrate, pH 5.0, and 100 mM NH_4NO_3 , 1 mM potassium sodium tartrate, 20 mM H_3PO_4 , pH 2.1. The flow rate was set at 1 ml min⁻¹. All of the optimised parameters used in the method are presented in Table 2. The validation parameters for the simultaneous determination of germanium species are presented in Table 3.

3.1.1 Influence of the injection volume, flow rate, and concentration of tartrate in the samples

The relation between injection volume and peak height is linear. The appropriate injection volume of the sample in HPLC improves signal intensity and influences retention times. The effect of the injection volume was checked over the range 40–150 μl . A volume of 40 μl was insufficient to achieve a good retention process. In contrast, injection with a volume of 150 μl resulted in peak broadening and the overlapping of signals. Problems with peak shape may be caused by mass overload, when the excess liquid sample is injected into the column. Therefore, an optimal value of injection volume of 100 μl was selected.

As an addition to the sample, the potassium sodium tartrate concentration was checked in the range of 80–120 mM. Based on Lehmann's research (Lehmann et al. 2019), a tartrate concentration of 80 mM was initially tested. However, under these conditions, the separation of analytes was not completely reached and the peaks of the organic forms of germanium were not fully divided. Increasing the concentration of this salt to 100 mM results in a slightly longer retention time of MMGe and makes the peak sharper and better separated from the DMGe signal. A 120 mM concentration of tartrate accompanied the flattening and spreading of the MMGe peak and worsened the separation. Therefore, a 100 mM tartrate concentration solution was used in further experiments. Figure 3 presents the chromatograms obtained when using different concentrations of potassium sodium tartrate.

The effect of the flow rate was tested at three levels: 0.4, 0.8 and 1.0 ml min⁻¹. Reduction in the retention times for DMGe and MMGe analytes was observed with the increase of the mobile phase flow rate (Fig. 3). The flow rate of the mobile phase was set at 0.8 ml min⁻¹ during chromatographic separation. The total time for separating germanium species was 12 min. All of the optimised parameters used by this method are presented in Table 2.

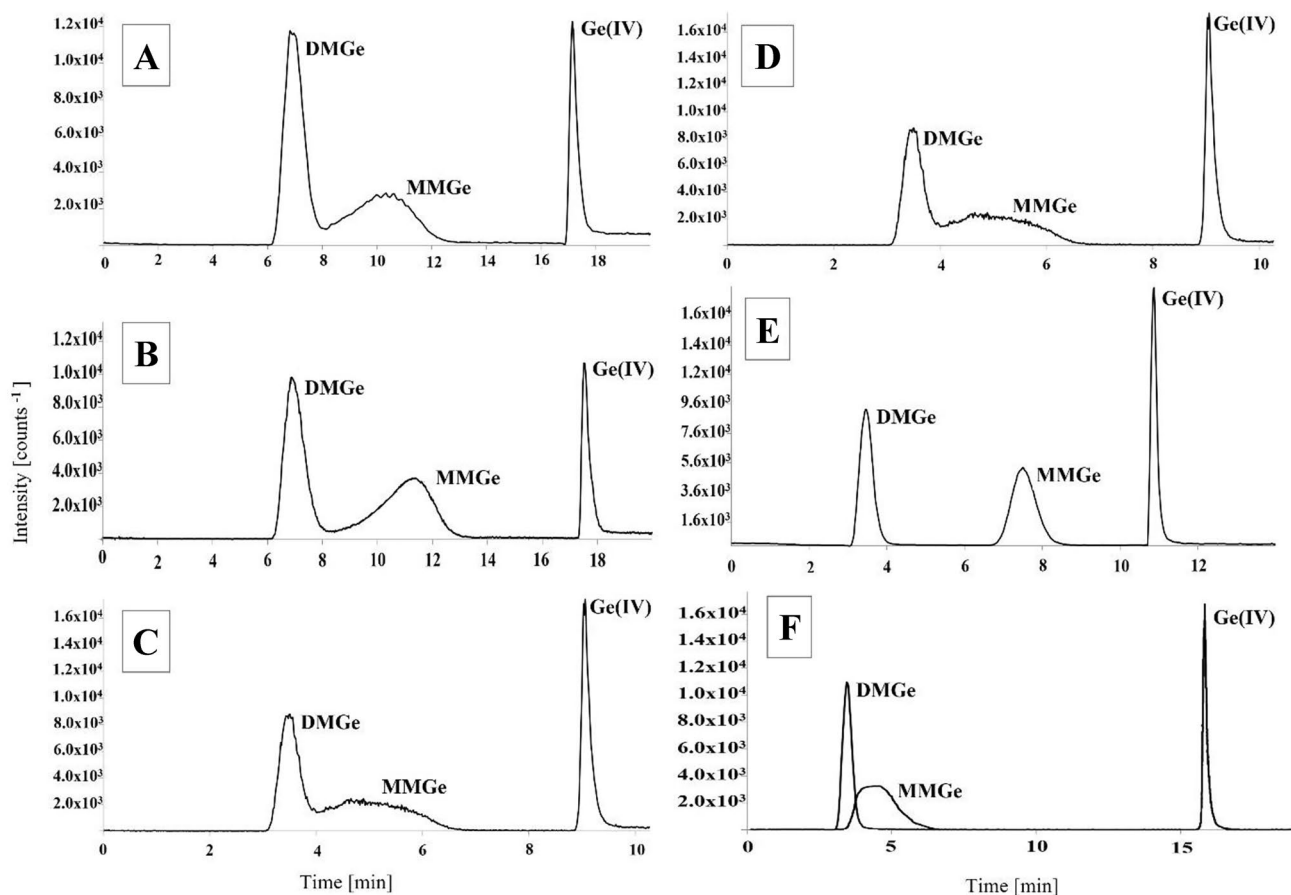


Fig. 3 Performing DMGe, MMGe and Ge(OH)₄ chromatographic separation under different conditions of tartrate concentration: **A** (80 mM); **B** (100 mM); **C** (120 mM) and flow rate: **D** (0.4 ml·min⁻¹); **E** (0.8 ml·min⁻¹); **F** (1.0 ml·min⁻¹)

3.2 Optimisation of soil sample extraction

The soils intended for germanium speciation analyses were extracted for 1, 2, 3 and 4 h. Extraction was initially assisted by shaking; however, the extraction efficiency was lower and so ultrasonic-assisted soil extraction was performed. The effect of extraction time on the degree of germanium leaching was investigated after 1, 2, 3, and 4 h. Figure 4 shows the results of germanium extraction from soils using various solutions (20 mM Na₂EDTA; 100 mM citric acid with 20 mM Na₂EDTA pH 3.8; 100 mM citric acid; 300 mM ammonium tartrate; 100 mM NH₄NO₃ with 1 mM potassium sodium tartrate; and 100 mM potassium sodium tartrate). This research has shown that the best extraction efficiency was obtained using 100 mM NH₄NO₃ with 1 mM potassium sodium tartrate acting as an extractant, washing out germanium from soils within 4 h.

3.3 Application of the developed Ge speciation method

The developed germanium extraction methods allowed for the analysis of soil samples taken from areas subjected to

anthropopressure from the WEEE plant in Katowice. The total content of metals and metalloids, including germanium and its species, are shown in Table S1. Figure 5 graphically shows the germanium concentration in the area surrounding the WEEE plant. The map of total Ge content was prepared using Surfer 8 software, based on 30 irregularly spaced soil sampling points. The map was created using gridding method which was point kriging with the default linear variogram. The regularly spaced, rectangular arrays of grid nodes, with a calculated Z value at each node, from irregularly spaced XYZ data were produced. Gridding calculated the Z values for grid nodes where data exists, as well as for grid nodes in the holes where no data exists, by the mathematical algorithms. However, Table 4 presents the results of soil sample speciation analysis after NH₄NO₃ with potassium sodium tartrate extraction. The results of the speciation analysis showed that, in the soils around the electrowaste processing plant, germanium was mainly present in Ge(VI) form. Methyl germanium derivatives were only found in a few soil samples. In five soil samples, apart from Ge(IV), there was a monomethyl derivative of germanium and, in

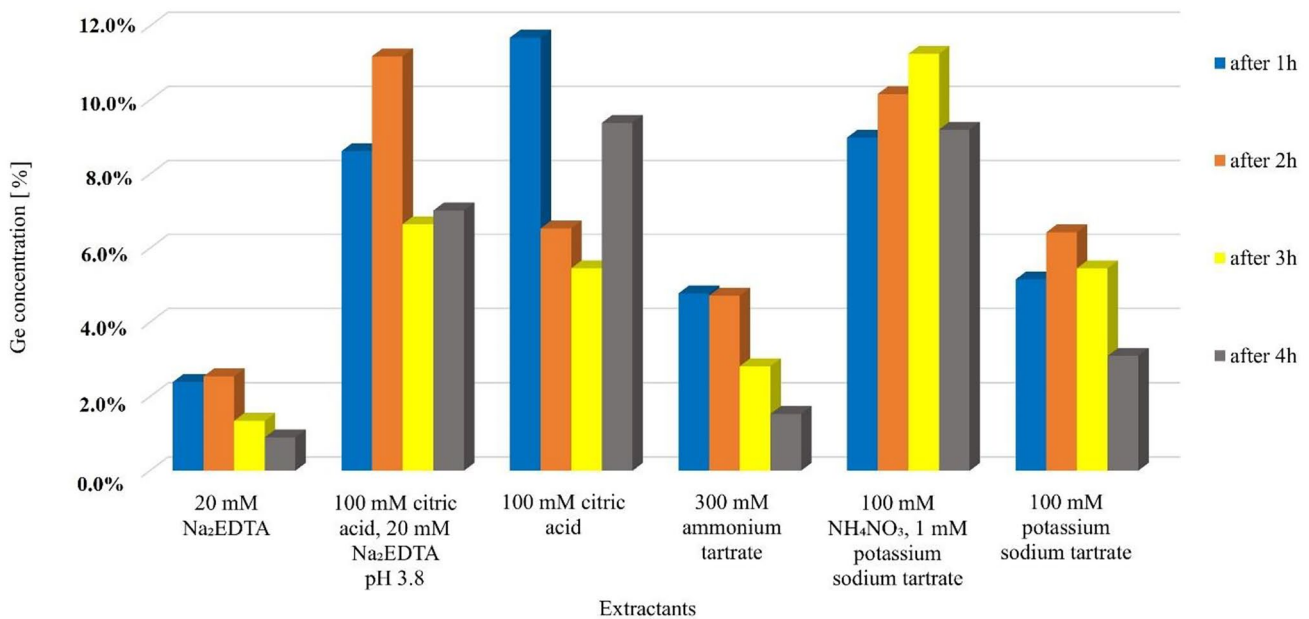


Fig. 4 Ultrasound assisted germanium extraction using various extractants

one sample, a dimethyl derivative of this element was found. It is difficult to relate the results obtained by this research to the content of methyl germanium forms in soils, due to the lack of available references. From the available information, it is known that methyl germanium derivatives are found in seawater. The presence of MMGe and DMGe in the soil is possible due to the biomethylation processes triggered by bacteria (Rosenberg 2009; Thayer 2002).

The highest concentration of germanium was almost 7.3 mg kg^{-1} . As shown in Fig. 5, an increased concentration of germanium occurred in soil samples located north of the electrowaste processing and sorting plant, which is consistent with the prevailing wind direction in this area (north, north-east). Figure 2b and c show the chromatograms of the soil

samples numbered 5 and 4, taken from the area surrounding the WEEE processing plant.

In sample No. 5, two forms of germanium were found, in the form of MMGe and inorganic germanium (iGe) but, in sample No. 4, DMGe and inorganic germanium species were found.

Most of the articles focussing on the study of methyl germanium derivatives focus on water samples. It is well-known that MMGe and DMGe are more abundant than iGe in seawater. The number of methyl species of germanium presents conservative ratios between them (García-Figueroa et al. 2021). The available research on methylgermanium derivatives in soil is particularly scarce and knowledge about its behaviour in a soil environment is even less. In our study, monomethyl derivatives were

Fig. 5 Spatial distribution of the total germanium content [mg kg^{-1}] in soil samples in the area surrounding the WEEE processing plant

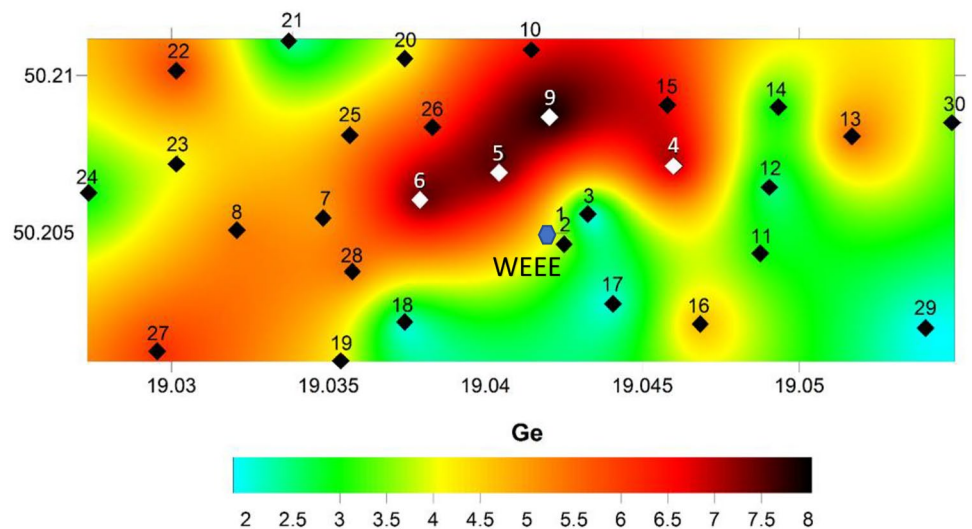


Table 4 Results of total germanium and germanium species (DMGe, MMGe, Ge(IV)) concentration in soil samples, Certified Reference Material NCS DC 73324 (China National Analysis Center for Iron and Steel, Beijing, China)

Sample No.	DMGe [mg kg ⁻¹]	MMGe [mg kg ⁻¹]	Ge(IV) [mg kg ⁻¹]	Total Ge [mg kg ⁻¹]	pH	Eh [mV]
1	< LOD	< LOD	0.9021	3.7095	4.56	312.2
2	< LOD	< LOD	0.6544	2.1510	4.32	356.9
3	< LOD	< LOD	0.5965	1.7016	3.67	297.1
4	0.1084	< LOD	0.2594	1.2035	3.54	299.8
5	< LOD	0.0703	1.6661	7.2897	4.52	295.4
6	< LOD	< LOD	0.9978	5.4741	5.37	290.5
7	< LOD	0.0060	0.9811	5.5650	5.23	355.8
8	< LOD	< LOD	0.4425	1.5922	4.33	376.8
9	< LOD	0.1480	1.4265	7.5580	4.99	313.9
10	< LOD	< LOD	1.3960	7.1388	4.29	366.2
11	< LOD	< LOD	0.3392	1.0183	4.67	298.5
12	< LOD	< LOD	0.5438	1.5382	4.64	286.2
13	< LOD	< LOD	0.8714	3.5065	7.50	216.5
14	< LOD	< LOD	0.9948	2.2817	5.87	324.9
15	< LOD	0.0599	0.2505	1.1504	3.85	384.5
16	< LOD	< LOD	0.8318	3.9194	5.60	305.2
17	< LOD	< LOD	0.5372	1.4726	5.82	354.8
18	< LOD	< LOD	0.6382	1.6265	5.59	342.9
19	< LOD	< LOD	0.5876	1.5290	5.43	362.4
20	< LOD	< LOD	0.6748	2.2822	5.29	376.2
21	< LOD	< LOD	0.5612	1.5732	5.36	327.9
22	< LOD	< LOD	0.7298	3.7457	5.47	263.5
23	< LOD	0.0642	1.2351	2.8761	4.72	287.1
24	< LOD	< LOD	0.9502	1.8752	4.36	290.3
25	< LOD	< LOD	0.6937	5.5939	3.83	302.9
26	< LOD	0.0325	0.3313	1.0408	7.41	224.3
27	< LOD	< LOD	0.8674	3.5080	3.43	425.5
28	< LOD	< LOD	0.3100	1.0452	4.56	312.2
29	< LOD	< LOD	0.6129	1.4871	5.81	348.0
30	< LOD	< LOD	0.9543	2.0191	5.87	326.9
CRM	< LOD	< LOD	0.6756	3.5430	6.29	269.5

LOD Limit of Detection, CRM Certified Reference Material

found in seven samples, while dimethyl derivatives were only found in one sample. It seems that the coexistence of methyl derivatives is less pronounced in soil than in water samples, and these forms may behave differently. The results of our work are consistent with those of Hirner et al. (2000), for contaminated soil. Both DMGe and MMGe were present in one soil sample, while only one of the forms was present in the other two samples. The occurrence of organometallic species in the environment is due to natural processes under specific criteria. However, anthropogenic activities also lead to local conditions enabling methanogenesis and biomethylation. It is worth mentioning that the content and emission potential of hazardous waste, such as industrial waste or electronic waste, have rarely been examined for organometallic compounds. It transpires that methyl germanium derivatives were found in soil samples taken from the area to the north

of the WEEE plant, which has the highest concentration of germanium in the study area. Figure 5 presents the spatial distribution of the total germanium contents of samples 5, 6, 9, 15, and 26, which are characterised by the highest concentrations of this element.

3.4 Results of element concentration and correlations between the germanium and other test parameters

Table S1 shows the total concentration of the elements in the soil samples. The germanium concentration ranges from 1.04–7.56 mg kg⁻¹. The analysed soil samples contain significant amounts of heavy metals: up to 1369 mg kg⁻¹ of lead and 593.3 mg kg⁻¹ of zinc.

The concentration of TCE is correlated with base metals (Filella and Rodríguez-Murillo 2017). The soil

magnetometry method has been successfully used in soil contamination studies, due to the correlation found between magnetic susceptibility and the content (often excessive) of metals and metalloids in soils (Rachwał et al. 2017a, b). Therefore, the use of magnetic susceptibility measurements to determine the locations of likely accumulations of TCE seems to be justified. The increased concentration of heavy metals is accompanied by an increase in magnetic susceptibility χ . The presence of an electrowaste collection, processing, and sorting plant increases the content of trace elements in the soil in the area surrounding this pollutant emitter. Research has shown that there is an increased concentration of tellurium (Grygoyć and Jabłońska-Czapla 2021), as well as thallium and germanium, in soil. Our research showed that the germanium concentration in the studied area was as high as $7.64 \text{ mg}\cdot\text{kg}^{-1}$, with an average concentration of $3.51 \text{ mg}\cdot\text{kg}^{-1}$. Other studies on Saxony soils indicated that the germanium concentrations in two different soils were 1.5 and $1.6 \text{ mg}\cdot\text{kg}^{-1}$ (Wiche and Heilmeier 2016). Germanium content in soils is influenced by the natural content of this element in ores, such as zinc sulphide ores, and the germanium content may be in the range $1\text{--}500 \text{ mg}\cdot\text{kg}^{-1}$ (Zhang and Xu 2018). A study of the area around the abandoned Sb-As-Tl Allchar mine, in the Republic of Macedonia, demonstrated that soils contained a minimal $0.046 \text{ mg}\cdot\text{kg}^{-1}$ and a maximal $0.390 \text{ mg}\cdot\text{kg}^{-1}$ of germanium. In these areas, despite the increased human activity, the content of germanium is low, which is related to the natural formation of ores in this area (Beceva et al. 2014). Research into the content of germanium in soil samples with a thickness of 2–4 cm, collected in eastern China, showed that the average concentration of this element in this climatic region is $1 \text{ mg}\cdot\text{kg}^{-1}$ (Yang et al. 2010). In contrast, the concentration of germanium in soil sampled from Maui (Hawaiian Island) was approximately $2\text{--}3 \text{ mg}\cdot\text{kg}^{-1}$ (Scribner et al. 2006); the concentration of this element in soil from the Island of Hawaii was as high as $5.6 \text{ mg}\cdot\text{kg}^{-1}$ (Kurtz et al. 2002). A study of French forest soil showed that germanium concentrations were in the range $1.9\text{--}2.3 \text{ mg}\cdot\text{kg}^{-1}$ (converted from $\text{nmol}\cdot\text{g}^{-1}$) (Cornelis et al. 2010).

Results obtained from the previous testing of electrical waste treated in the WEEE facility, clearly showed that germanium content was the highest in the smallest fraction ($< 0.1 \text{ mm}$) for all types of examined electrowaste elements. The content of Ge differed, depending on the type of electronic components and the main carriers of germanium were photo-resistors ($2.59 \text{ mg}\cdot\text{kg}^{-1}$) (Willner et al. 2021). This study confirms that there is a significant impact of the processing of electrowaste (with a high content of germanium) on the increasing concentration of this element in the areas surrounding WEEE plants.

As part of this study, soil samples were also collected in areas not subjected to the pressure of e-waste processing, in an agricultural area in the vicinity of Lublin City (Poland).

The average concentration of germanium in this area was $1.84 \text{ mg}/\text{kg}$. Research has shown that the germanium contamination of the area surrounding the electrowaste processing plant is caused by dust rising from the emitter, as indicated by the higher concentration of germanium in the prevailing wind direction in the area.

To check the correctness of the methodology for determining the concentration of elements in the soil, a certified reference material (NCS DC 73324) was used. Table S1 shows the concentration values of elements in the certified reference material and those measured in our research. Element recovery was in the range 91–110% and varied, depending on an individual element. The concentrations of the measured elements were in satisfactory agreement with the certified values.

The obtained results allowed the calculation of the correlation coefficients and created a correlation matrix, which is presented in Table S2. Many weak correlations were found between the concentration of germanium in soils and other elements, such as As, Sb, Ni, Sr, Cr, Al, Fe, and Mn. Correlation testing (Table S2) of germanium content with the pH and redox potential of the studied soils did not show a significant relationship. pH and redox potential were variable in a wide range. No strong correlation was found between soil pH, Eh and germanium concentration. The results also confirmed the correctness of the application of soil magnetometry for classifying soil sampling sites due to the correlation of magnetic susceptibility with the majority of heavy metals (Ni, Zn, Pb, Cr, Mo). The use of soil magnetometry to identify areas of heavy metal accumulation was used in the studies carried out by Rachwał et al. (2015, 2017a, b). Our research has confirmed that this method is also applicable to detect technology critical elements such as germanium. Soil samples with the highest content of germanium had very high magnetic susceptibility and there is a correlation between these parameters (Table S2).

4 Conclusion

In the studied area, germanium entered the environment during the recovery of electrowaste and it accumulated with other metals in the soil, mainly in the topsoil. Because of its widespread use in the semiconductor industry, there is a large amount of germanium in the waste at electrowaste treatment plants. This was confirmed by our previous research, in which the TCE content in electrowaste was determined (Willner et al. 2021). Germanium in electrowaste occurs as iGe, so the methyl derivatives found in the soil are most likely the result of methylation processes taking place in the soil itself. The highest concentration of germanium occurred in soil samples located north of the electrowaste processing and sorting plant, which is consistent with the prevailing wind direction in this area. Based on the obtained results, it can be stated that the most common germanium species, in

areas under the pressure of a WEEE processing plant, was an inorganic form of germanium (Ge(IV)). However, in several samples with the highest concentration of this element, organic germanium species, such as MMGe and DMGe, were also found. The optimisation of the germanium extraction and speciation methodology in soil samples allowed for environmental studies of contaminated soils. The best extraction efficiency was obtained using 100 mM NH_4NO_3 with 1 mM potassium sodium tartrate as an extractant, washing out germanium from soils within 4 h. Optimised separation conditions enabled separation of the three germanium species (monomethylgermanium (MMGe), dimethylgermanium (DMGe), and Ge(IV)) using the Dionex IonPack™ As9-HC column. The use of IC-ICP-MS hyphenated techniques makes it possible to carry out a quick speciation analysis of a soil extract within 12 min. By using the ICP-MS spectrometer with a DRC-e reaction chamber, the interferences that have a negative effect on the determination of germanium with this technique are eliminated.

Our research confirmed the legitimacy of using soil magnetometry to determine the sampling sites of soils characterised by increased concentrations of metals and TCE. Soil samples with the highest content of germanium had very high magnetic susceptibility and there is a correlation between these parameters.

Due to the growing demand for new technologies, the global consumption of TCE, including germanium, has increased. In addition, drastic developments in the electrical and electronic industry, rapid consumption and the ‘aging’ of electrical and electronic equipment (requiring regular replacement) results in an increased amount of WEEE. For this reason, research on the impact of processes related to the recovery of electronic waste on various elements of the environment, including soil, is important and needed.

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Sample availability Samples of the compounds are available from the authors.

Declarations

Research with no involving human participants and/or animals The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Financial interests The authors declare they have no financial interests.

Ethical approval The Authors confirm that the manuscript entitled “Germanium speciation study in soil samples taken from an area associated with the storage, processing, and recovery of electrowaste” has not been published previously and is not under consideration for publication elsewhere.

Consent to participate All authors agree to participate.

Consent to publish All authors declare their consent to publication.

Conflict of interest The authors declare no conflict of interest.

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