Final Draft

of the original manuscript

Klein, O.; Zimmermann, T.; Pröfrock, D.:

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In: Journal of Analytical Atomic Spectrometry. Vol. 36 (2021) 7, 1524 - 1532.

First published online by RSC: 19.05.2021

https://dx.doi.org/10.1039/D1JA00088H

Improved Determination of Technologically Critical Elements in Sediment digests by ICP-MS/MS using N_2O as Reaction gas

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Keywords

Environmental analysis, sediment reference materials, spectral interference reduction, ultra-trace analysis

Abstract

The investigation of technologically critical elements (TCEs) as emerging pollutants is a constantly growing field of environmental research and societal concern. Nevertheless, existing data for most TCEs are still unsatisfactory for an accurate assessment of their potential (eco)toxicological effects on humans and the environment. The limited availability of data mainly results from the technical challenging analysis of selected TCEs. Low concentrations of TCEs in environmental matrices (μg kg^{-1} or lower) and the associated complex and time-consuming sample preparation pose the greatest challenges. This work aims at developing a new ICP-MS/MS-based multi-elemental approach targeting the analysis of all major TCEs (Sc, Ga, Ge, Nb, In, Te, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Yb, Lu, Ta) in sediment, which represents one of the most important matrices for environmental research. N_2O is applied as reaction gas to overcome possible spectral interferences during ICP-MS/MS analysis. The use of N_2O as reaction gas for ICP-MS/MS analysis enabled higher oxide-product ion yields for many TCEs in comparison to the frequently used O_2 cell gas. Hence, selectivity and sensitivity of the method were improved. The presented multi-element method using N_2O as reaction gas achieved *LOD*s between 0.00023 μg L^{-1} (Eu) and 0.13 μg L^{-1} (Te) for all analyzed TCEs. Likewise, for all analyzed elements, except for Te, recoveries between 80% and 112% were obtained for at least one of the analyzed reference materials (GBW 07313, GBW 07311, and BCR-2).

Introduction

Technologically critical elements (TCEs) are defined as elements or minerals, which can be considered socially and economically critical, due to possible supply risks or supply restrictions. Despite the potentially limited and critical supply situation, TCEs play a crucial role for today's high tech applications.[1-4] TCEs are used in various industrial sectors including, the information technology sector, the transport sector (electromobility), and the field of renewable energy production (wind power, solar power etc.)[5, 6]. However, they are also present in almost every multimedia device and consequently becoming mandatory in every single household. Despite the increasing interest in and usage of TCEs in modern industries, some of these elements (e.g. Ga, Ge, Nb, In, Te and Ta) still show a lack of knowledge regarding their potential impact on the environment.[1, 7] Up to now, little is known about the (eco)toxicity of many TCEs and their respective environmental species. It is believed, that the rising usage of TCEs may lead to unforeseen negative environmental impacts within the next years or decades.[7-9] Due to the challenging analytical determination of selected TCEs recent environmental studies still show a deficiency of related data.[10] Consequently, there is an increasing demand for adequate and reliable analytical methods for the determination of TCEs in typical environmental matrices such as water, biota or sediments.[2, 7]

In the first place, the analysis of TCEs in environmental samples is challenging due to their low natural abundances (e.g upper crust abundance of Ta is about 0.9 ng kg^{-1}). This fact often leads to difficulties regarding their quantification, resulting in expensive and time-consuming sample preparation processes.[7, 8, 11] Additionally, most methods are only suitable for the analysis of a subset of the TCE group or the respective sample preparation processes are confined to single elements.[12-14] This situation necessitates new analytical methods for the determination of multiple TCEs in environmental samples without the need for extensive sample preparation.[7]

In environmental analysis, sediment or mineral samples are routinely analyzed. Sediments in particular are considered a time record of environmental changes due to their potential to accumulate contaminants over time. As sediments reflect the time-integrated status of the aquatic environment, they are a powerful indicator to detect environmental changes in rivers, estuaries or coastal areas over space and time.[15-17] Therefore, the analysis of elemental mass fractions in sediments is a common method for the assessment of long-term or emerging contamination of aquatic systems. Nevertheless, acid digests of sediment samples also

represent an extremely complex sample matrix, often hindering the precise determination of trace and ultra-trace analytes such as TCEs.[17]

Inductively coupled plasma mass spectrometry (ICP-MS) has proven to be the method of choice for the determination of trace and ultra-trace elements in various environmental matrices[18-20]. ICP-MS allows for low detection limits (*LOD*) combined with high sample throughput and outstanding multi-elemental capabilities. However, TCE analysis via ICP-MS may be impeded by spectral interferences. These inferences are mainly isobaric, doubly charged, or polyatomic ions with the same *m*/*z* as the analytes of interest. Notwithstanding, the approach of inductively coupled plasma tandem mass spectrometry (ICP-MS/MS) allows to overcome interferences by using different reaction or collision gases (e.g. O_2 or NH_3) and a second quadrupole mass filter.

Various spectral interferences hampering the accurate determination of TCEs have been reported (e.g. $^{142}Nd^{2+}$, $^{142}Ce^{2+}$, and $^{141}Pr^{2+}$ for $^{71}Ga^{+}$ or $^{115}Sn^{+}$ for $^{115}In^{+}$).[2, 21] The quantification of some TCEs is particularly challenging, if spectral interferences are created by other targeted analytes, e.g. the determination of Ge ($^{72}Ge^{+}$) suffers from doubly charged interferences of Nd ($^{143}Nd^{2+}$, $^{144}Nd^{2+}$) and Sm ($^{144}Sm^{2+}$). Recent work proved that numerous interferences (e.g. of the rare earth elements (REE)) can be resolved by using ICP-MS/MS and O_2 as reaction gas.[22-24] Noteworthy, it has been demonstrated that the formation of $REEO^{+}$ is significantly fostered by using N_2O instead of O_2 as a reaction gas; thus, improving sensitivity and *LODs*.[25] Advantages of N_2O over O_2 in terms of serving as reaction gas are the preferred O transfer reaction of N_2O to other ions. Due to the lower O-binding energy of N_2O reaction, enthalpies for many analyses can be reduced. Herewith, higher reactions rates can be achieved when using N_2O.[24, 26] For instance, N_2O enables higher formation rates of the M+16 or M+32 product ions, allowing to increase sensitivity and selectivity for elements like Ge, Eu, or Yb by enabling to measure their respective oxides.[25, 27-29]

The aim of this work was the development of a new ICP-MS/MS-based method for the determination of TCEs with a special focus on Ga, Ge Nb, In, Te and Ta in sediment digests, using N_2O as oxidizing reaction gas to selectively eliminate possible spectral interferences of these analytes, to allow for a more selective and sensitive measurement.

Experimental

Reagents and standards

All preparatory laboratory work was performed in a class 10,000/1,000 clean room. Type I reagent grade water (>18.2 MΩ cm) was obtained from an ultra-pure water system consisting of an Elix 3 module (Merck Millipore, Darmstadt, Germany), a Milli-Q element module (Merck Millipore, Darmstadt, Germany), and a Q-POD element (Merck Millipore, Darmstadt, Germany). Analytical grade HNO_3 (65% *w*/*w*, Fisher Scientific GmbH) and analytical grade HCl (30% *w*/*w*, Carl Roth GmbH + Co. KG, Karlsruhe, Germany) were further purified either by double sub-boiling in perfluoralkoxy-polymer (PFA)-subboling stills (DST-4000 & DST-1000, Savillex, Minnesota, USA) operated under clean room conditions. HBF_4 (38% *w*/*w*, Chem-Lab, Zedelgem, Belgium) was used in ultra-pure quality for sample digestion without any further purification.

Single and multi-element solutions were prepared, using either single element standards (Carl Roth GmbH, Karlsruhe, Germany or Sigma Aldrich, Missouri, USA) or custom-made multi-element standards (all traceable to NIST standards) of different compositions (Inorganic Ventures, Christiansburg, USA).

The reference marine sediment GBW 07313 (National Research Centre for Certified Reference Materials, Beijing, China), the reference stream sediment GBW 07311 (National Research Centre for Certified Reference Materials), and Basalt reference material BCR-2 (United States Geological Survey Certificate of Analysis, Denver, USA) were used for method development and validation.

Instrumentation and measurement procedures

Measurements were conducted using an Agilent 8900 ICP-MS/MS (Agilent Technologies, Tokyo, Japan) coupled to an ESI SC-4 DX FAST discrete autosampler (Elemental Scientific, Omaha, Nebraska, USA) equipped with an ultra-low penetration air (ULPA) filtration unit (Elemental Scientific, Omaha, Nebraska, USA). O_2, N_2O and the no Gas measurement modes were employed during all experiments. However, the instrumental setup only allows measuring with either O_2 or N_2O since both gases share the same recommended cell gas line (cell gas line 4 for corrosive gases). Therefore, if necessary, measurements were conducted two times to gather information for both the O_2 and the N_2O mode. For each measurement, the instrument

was optimized using a tune solution containing Li, Co, Y, Ce, and Tl (10 µg L^{-1}). Optimal tuning conditions are enumerated in Table 1. An external calibration covering a concentration range from 0.1 µg L^{-1} to 100 µg L^{-1} (stabilized in 3% (*w*/*w*) HNO_3 and 1% (*w*/*w*) HCl) for all analytes was used for quantification of each element. Each solution for optimization and quantification was prepared from custom-made multi-element standards (Inorganic Ventures, Christiansburg, USA) on a daily basis. To monitor potential carry-over effects wash blanks of 2% (*w*/*w*) HNO_3 were measured after each sample triplicate.

Table 1 Standard ICP-MS/MS instrument and plasma parameters

Parameter	**Single MS**	**MS/MS**	**MS/MS**
Used Cell Gases	None	O_2	N_2O
Nebulizer	Self-aspirating PFA MicroFlow	Self-aspirating PFA MicroFlow	Self-aspirating PFA MicroFlow
Cell gas flow	None	20%[1]	10%[1]
Spray chamber Temperature	2°C	2°C	2°C
Interface cones	Nickel	Nickel	Nickel
RF Power	1550 W	1550 W	1550 W
RF Matching	1.80 V	1.80 V	1.80 V
Nebulizer flow rate	1.07 L min^{-1}	1.10 L min^{-1}	1.07 L min^{-1}
Makeup gas flow rate	0.12 L min^{-1}	0.11 L min^{-1}	0.12 L min^{-1}
Integration time	0.1 s	0.1 s	0.1 s
Extract lens 1	-11.8 V	-7.6 V	-11.5 V
Extract lens 2	-240.0 V	-215 V	-205.0 V
Omega bias	-150.0 V	-130 V	-130 V
Omega lens	7.6 V	5.8 V	6.6 V
Q1 entrance	-50.0 V	-50.0 V	-50.0 V
Q1 exit	1.0 V	3.0 V	3.0 V
Cell focus	-4.0 V	3.0 V	2.0 V
Cell entrance	-40 V	-40 V	-40 V

[1] relative to approx. 1.5 mL min^{-1} at 100%

Cell exit	-51 V	-51 V	-51 V
Deflect	15.2 V	7.8 V	8.2 V
Plate bias	-50 V	-50 V	-50 V
OctP bias	-8.0 V	-8.0 V	-0.5 V
Axial Accelaration	0.0 V	1.0 V	1.0 V
OctP RF	130 V	160 V	150 V
Energy discrimination	5.0 V	-5.0 V	-5.0 V

Comparison between O_2 and N_2O as a reaction gas

To compare the effectiveness of O_2 and N_2O as the oxidizing reaction gases for Ga, Ge, Nb, In, Te, REEs, and Ta product ion scans for each analyte were conducted. For this purpose, a multi-element solution (100 µg L^{-1}) was measured using the product ion scan option of the instrument. Here the first quadrupole (Q1) is adjusted to a specific *m*/*z*, allowing only ions of this *m*/*z* to enter the reaction cell. The second quadrupole is set to scan the entire spectrum from *m*/*z*=2 to *m*/*z*=275, thus measuring any potential product ions that may form in the reaction cell. For this kind of measurement, every analyte was measured on its recommended isotope to keep potential spectral interferences as low as possible. After each measurement, the ICP-MS/MS system was flushed with the respective reaction gas (O_2 or N_2O) by using a custom-made-flushing setup consisting of two 3 port valves allowing to flush the entire gas line bypassing the ICP-MS/MS. The gas lines were flushed for about half a minute using the respective gas. Afterwards, the cell was flushed for about 15 min setting the mass flow controller at 100% of the possible gas flow rate. For quantification of product ion formation rates, the relative formation rates were calculated by dividing the observed signal intensity of the product ion by the on-mass reference signal in the respective measuring mode.

Effectiveness of N_2O to reduce possible interferences on Ga, Ge, Nb, In, Te, and Ta

The effects of possible interferences (mainly doubly charged and oxide ions) on the determination of Ga, Ge, Nb, In, Te, and Ta, as well as the effectiveness of interference reduction by N_2O as the reaction gas, were analyzed by measuring single element standards (100 µg L^{-1}) or single-element solutions (*a*) spiked with their respective interfering elements (*i*) at ratios of *a*/*i*=1:10 and *a*/*i*=1:100. Within this context our work focused on these six

elements since earlier studies already emphasized that the measurement of REE as $REEO^+$ will significantly decrease potential interferences mainly caused by other $REEO^+$.[22-25] Each solution was measured both in the no gas single quadrupole mode and in the MS/MS mode with N_2O as a reaction gas. Relative signal intensities were used to quantify the influence of different interferences and the effectiveness of interference reduction. The corresponding relative signal intensities were calculated based on the signal of the unspiked single element solution in the respective measuring mode (no gas or N_2O) as reference.

Digestion procedure

The digestion of each sediment reference material was accomplished via microwave-assisted acid digestion using either a MARS Xpress or a MARS 6 (CEM Corp., Kamp Lintfort, Germany) respectively following the digestion protocol developed by Zimmermann *et al.* (2020).[17] Briefly 50 mg of sediment were digested using a mixture of 5 mL HNO_3, 2 mL HCl and 1 mL HBF_4 at 180°C for 300 min.

Validation of optimized method using certified (sediment) reference materials

Validation of the optimized method was carried out by means of the reference materials GBW 07313, GBW 07311, and BCR-2. All analytes were measured using the single MS mode with no additional cell gas, and using the MS/MS with N_2O in a single acquisition.

Data processing and calculations

Multi-element data was processed using MassHunter version 4.4 (Agilent Technologies, Tokyo, Japan) in combination with a custom-written Excel© spreadsheet. Using this spreadsheet, the respective limit of detection (*LOD*) ($3\times SD$) and limit of quantification (*LOQ*) (*3*LOD*) of the method , were calculated based on the digestion blanks (n=6), as described by MacDougall *et al*..[30] Furthermore, expanded uncertainties with a coverage factor of 2 (U, k=2) for each element present in the different reference materials were calculated using a simplified *Kragten* approach following Reese *et al.(2019)*.[31, 32] For this purpose, the measurement precision of the samples, as well as the reproducibility of multiple digests were taken into account.

The significant number of digits of mass fractions are given according to GUM and EURACHEM guidelines, whereby the uncertainty determines the significant number of digits to be presented with the value.[33, 34]

Results and Discussion

Product ion scans of selected TCEs using O_2 and N_2O as reaction gases

Figure 1 gives an overview of selected TCEs (Ga, Ge, Nb, In, Te, La, Eu, Yb, Lu, Ta) and their relative oxide formation rates. Here Ga, Ge, Nb, Te and Ta represent TCEs with no information on possible product ions using N_2O as reaction gas, while La, Eu, Yb and Lu were selected to represent the REEs. Within this context La and Lu represent members of the light REE (LREE) and heavy REE (HREE), respectively. Eu and Yb were included since both of them are known to have low oxide formation rates when using O_2 as reaction gas.[29] Additional data for other REEs can be found in ESI Table A.1. In Figure 1 color-coded columns display the M, M+16 as well as M+32 formation rates for the O_2 and N_2O measuring mode. Hence, it is possible to directly compare the respective sensitivity for each ion. Scanning of possible product ions revealed the preferable formation of oxides with a mass shift of M+16 or M+32 for most of the tested analytes except for Ga, In and Te for which no significant oxide formation was observed. Despite the insignificant oxide formation of Ga, In, and Te, Figure 1 illustrates absolute signal intensities (cf. ESI Tabel A.1) showing that the usage of N_2O led to significantly higher signal intensities for the M^+ ion for each of the three elements. This indicates that a more sensitive measurement of Ga, In and Te could be possible when using N_2O instead of O_2.

The other analytes showed oxide formation rates ranging from 0.1 (YbO^+) for O_2 as reaction gas to 1330 (LaO^+) for N_2O as reaction gas. It becomes evident that Ge, La, Eu, Yb, and Lu beared the highest relative oxide formation rates at M+16 ranging from 1.5 (Yb) to 1330 (La) when N_2O was used as a reaction gas. However, the same elements only reached relative formation rates of 0.1 (Yb) to 320 (La) once O_2 was used. This indicates that N_2O induces a better O transfer for these five elements. This tendency was confirmed for all other REEs (ESI tables A.1) except for Pr, Nd, Tb, Ho and Er. The improved oxide formation rate of N_2O was particularly evident for the formation of EuO^+ and GeO^+. With respect to both elements, the usage of O_2 as oxidation gas resulted in relative signals of 0.3 (EuO^+) and 0.5 (GeO^+) while formation rates of 61 and 82 were achieved by using N_2O.

Nb and Ta preferred to form M+32 ions for both O_2 and N_2O as reaction gases. Figure 1 shows relative formation rates of NbO_2^+ for both O_2 (161) and N_2O (193), indicating that detection of Nb clearly benefits from utilization of both gases. Similarly Ta preferred to form dioxides at m/z = 181+32 with relative formation rates of around 207 (O_2) and 40 (N_2O) indicating that

other products (mostly N_2O cluster) are formed as well.[28] However, further measurements elucidated that the measurement of Ta as TaO^+ at m/z = 197 enables a more stable measurement despite lower sensitivity. Regarding all the above-mentioned elements, it is possible to exploit the mass shift mode to reduce or eliminate possible matrix-related spectral interferences.

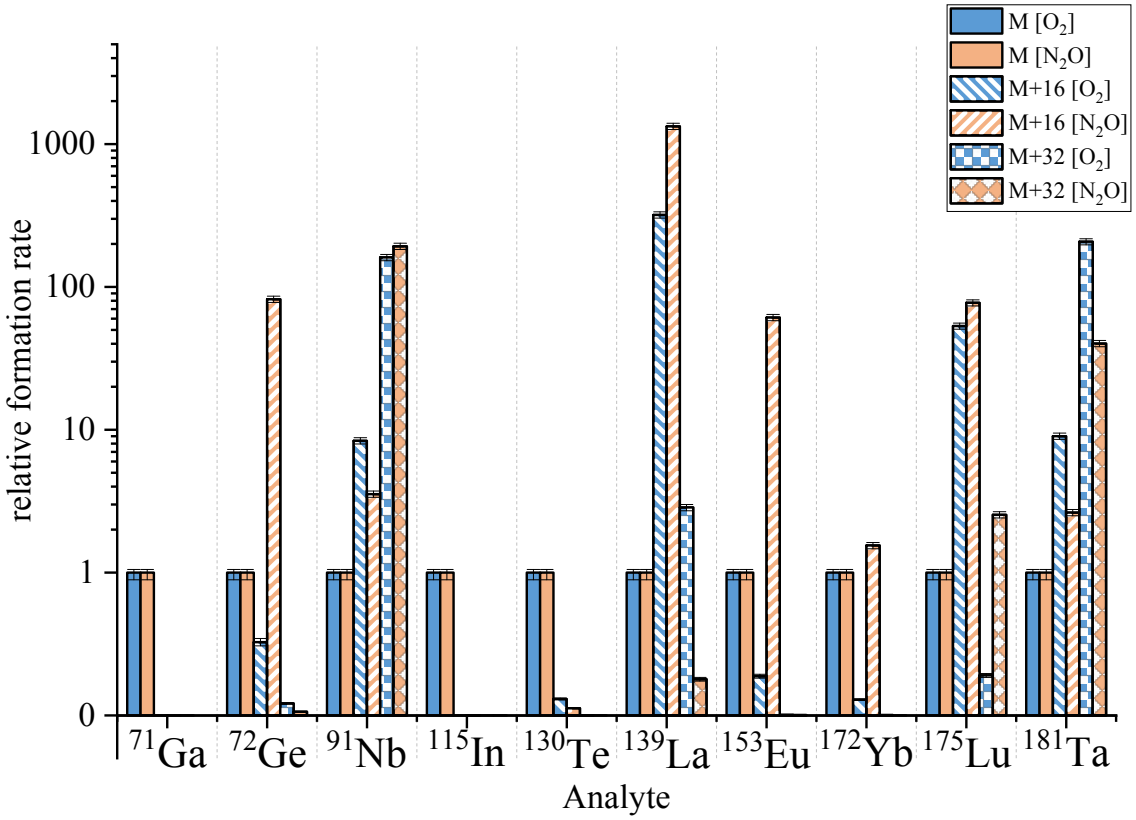

Figure 1 Comparison of the relative oxide formation rates for Ga, Ge, Nb, In, Te, La, Eu, Yb, Lu, and Ta and their main product ions in O_2 (blue) and N_2O (orange) measuring mode. All relative oxide formation rates refer to the absolute signal intensities in CPS of the respective element measured in the given gas mode.

Elimination of the most abundant interferences on Ga, Ge, Nb, In, Te and Ta using N_2O as a reaction gas

Detection of TCEs often suffers from spectral interferences making a precise measurement at sub-mg kg^{-1} levels very challenging. Therefore eliminating these interferences in order to improve the sensitivity and selectivity of the measuring method is inevitable. Table 2 gives a short overview of the respective TCEs (Ga, Ge, Nb, In, Te and Ta) and their most abundant or often occurring interferences when analyzing environmental matrices. Since previous studies already have shown, that the measurement of REE as $REEO^+$ can reduce the negative effects of interfering elements (mainly other $REEO^+$) and the fact that N_2O leads to better oxide

formation for the REEs the following section focuses on the improved determination of the TCEs Ga, Ge, Nb, In, Te and Ta.

Table 2 Overview of measured isotopes of Ga, Ge, Nb, In, Te and Ta and their most abundant spectral interferences

Analyte	Interference
^{71}Ga	$^{142}Nd^{2+}$, $^{142}Ce^{2+}$, $^{141}Pr^{2+}$, $(^{55}Mn^{16}O)^{+}$, $(^{40}Ar^{31}P)^{+}$
^{72}Ge	$^{143}Nd^{2+}$, $^{144}Nd^{2+}$, $^{144}Sm^{2+}$, $(^{56}Fe^{16}O)^{+}$, $(^{40}Ar^{32}S)^{+}$, $(^{40}Ca^{16}O_2)^{+}$
^{93}Nb	$^{186}W^{2+}$, $(^{40}Ar^{53}Cr)^{+}$
^{115}In	$^{115}Sn^{+}$, $(^{40}Ar^{75}As)^{+}$
^{130}Te	$^{130}Ba^{+}$, $^{130}Xe^{+}$, $(^{114}Cd^{16}O)^{+}$
^{181}Ta	$(^{165}Ho^{16}O)^{+}$

Figure 2 compares the relative signal intensities of single element solutions of Ga, Ge, Nb, In, Te and Ta in the no gas and N_2O measurement modes. Besides, the respective analyte solutions (*a*) were spiked with interfering elements (*i*) at two different ratios (*a*/*i*=1:10 and *a*/*i*=1:100). This setup enabled the evaluation of the possible influence of interferences as summarized in Table 2. It provides a good comparison of possible sensitivity or selectivity enhancements when using N_2O as a reaction gas.

Figure 2a shows that the presence of Nd and Ce in a ratio of 1:100 has a large effect on the signal intensity of ^{71}Ga in the no gas mode. The intensity increased by almost 27% (Nd) and 16% (Ce), which is caused by the formation of doubly charged Nd^{2+} and Ce^{2+} in the plasma. In the N_2O MS/MS mode, these interferences can be overcome since Nd^{2+} and Ce^{2+} are no longer able to pass the second quadrupole, as they will react to MO^{2+} or MO^{+} in MS/MS mode, thus ensuring an interference-free measurement on *m*/*z*=71 for Ga. Whereas the potential interference caused by Pr^{2+} proved to be insignificant in the N_2O mode for the tested elemental ratios.

A similar pattern was observed for ^{72}Ge (Figure 2b). In this case, Nd (1:100 ratio) may lead to an increasing signal of ^{72}Ge when measuring in the no gas mode. In contrast, Sm^{2+} seems to have no significant influence on the determination of ^{72}Ge due to the lower isotopic abundance of ^{144}Sm. Measurements of ^{72}Ge and the accordingly spiked Ge samples investigated in the N_2O mode revealed the possibility to eliminate Nd^{2+} interferences by detection of $^{72}Ge^{+}$ as

$^{72}Ge^{16}O^+$ (mass shift from *m*/*z*=72 to *m*/*z*=88). While, Nd^{2+} will be discriminated as $^{144}Nd^{16}O_2^+$ and $^{144}Nd^{16}O^+$ or as $^{143}Nd^{16}O_2^+$ and $^{143}Nd^{16}O^+$, respectively.

Figure 2c shows, that W may hamper an accurate analysis of Nb either in the no gas or N_2O mode. A W induced signal suppression can be observed for both measuring modes leading to the hypothesis that the signal suppression may take place inside the ion source itself. Even though the interference effect of W on Nb could not be improved by using N_2O as reaction gas, it is safe to say that the analysis of Nb still benefits from the MS/MS mode as W/Nb in environmental matrices may be < 5 leading to a non-significant change in the measured intensities. Furthermore, a measurement of Nb as NbO_2^+ will also help to overcome other possible polyatomic interferences like $(ArMn)^+$, $(ArFe)^+$, or $(ArCr)^+$.

As shown in Figure 2e, the determination of ^{130}Te is massively impaired by the isobaric interference of ^{130}Ba in the no gas mode. At a spike ratio of 1:100, an increase of the signal by factor 2 was observed. In the N_2O mode, Ba^+ reacts to BaO^+, which allows an interference-free measurement of ^{130}Te.

Figure 2d shows that both the no gas and the N_2O mode will lead to a ^{115}Sn interference-free detection of ^{115}In up to a spike ratio of at least 1:10. In both modes, the signal intensity increased slightly for a spike ratio of 1:100. This can be expected due to the low natural abundance of ^{115}Sn (0.34%) and high natural abundance of ^{115}In (95.7%).The effect of Ho on the measurement of ^{181}Ta showed an unusual behaviour. Here the lower spiked solution (1:10) showed a significant intensity increase for Ta while the higher spiked solution showed a signal reduction. This pattern is evident for both measuring modes (no gas and N_2O) again leading to the conclusion that in that the effect may take place in the ion source.

The N_2O MS/MS mode shows the potential to significantly reduce the influence of isobaric and polyatomic inferences for the elements Ga, Ge and Te. This also offers the possibility to analyze more abundant isotopes. Thus, leading to improved sensitivities e.g. in the case of ^{130}Te. For Nb, and Ta little to no improvement can be observed for the tested interferences (W, Sn and Ho), but we are convinced, that the measurement in the N_2O mode will still lead to improved results since other polyatomic interferences will be eliminated by the use of the mass shift mode.

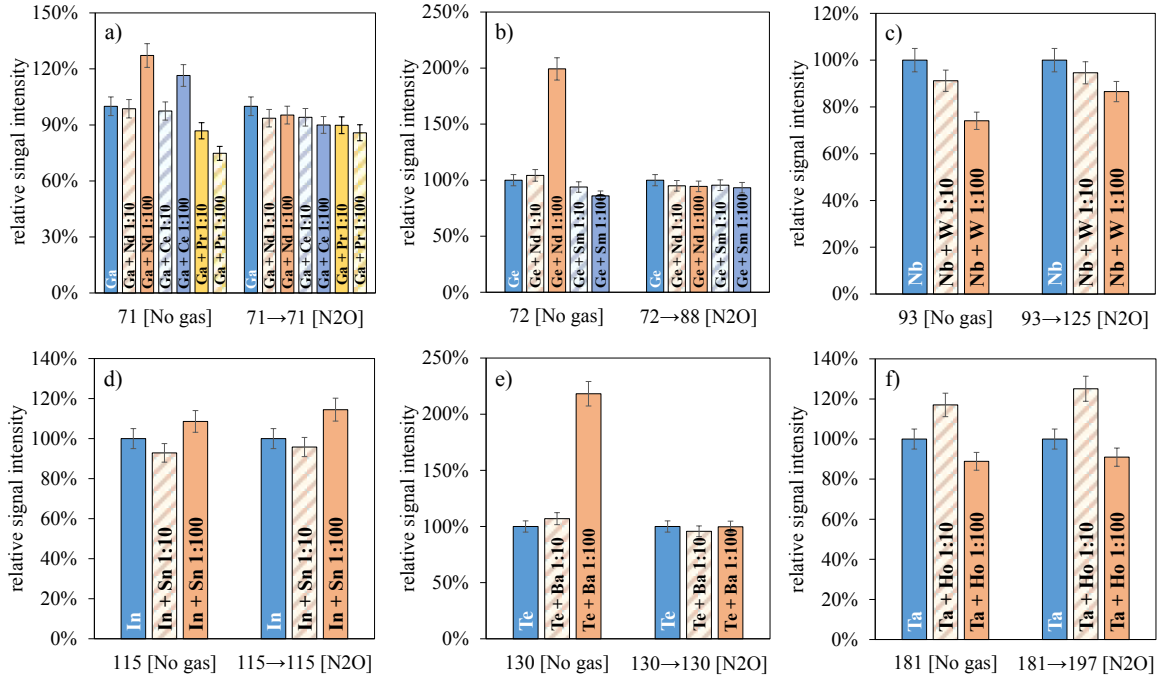

Figure 2 Comparison of the relative signal changes in the no gas mode and N_2O mode of a) Ga, b) Ge, c) Nb, d) In, e) Te, and f) Ta in the presence of their most frequent interferences, spiked in different ratios (1:10 and 1:100). All relative signals in percent refer to the absolute signal in CPS of the corresponding measurement of the single element solution in the respective measurement mode.

Limits of quantification and recoveries of TCEs in digests of certified reference materials

Acid digests of the reference materials BCR-2, GBW 07311, and GBW 07313 were measured using the developed method to determine the accuracy and recoveries for the individual analytes. The provided *LOD*s and *LOQ*s are based on six method blank values. Table 3 shows a comparison of the calculated *LOD*s for each measured TCE in single MS no gas mode and in MS/MS mode using either O_2 or N_2O.

The measurement of TCEs in the MS/MS modes (O_2 and N_2O) led to an improved or at least similar *LOD* compared to the no gas mode. Only La, Sm, Tb, Dy, Er and Ta show lower *LOD*s in the no gas mode. Even though these six elements do not show improved *LOD*s in one of the MS/MS modes it is highly recommended to use the mass shift mode since it ensures the removal of earlier discussed spectral interferences. Additionally, it is evident that for these elements the N_2O mode often provides *LOD*s within the same range as the *LOD*s of the no gas mode (e.g. La: $LOD_{no\ gas} = 0.006\ \mu g\ L^{-1}$, $LOD_{N2O} = 0.006\ \mu g\ L^{-1}$ or Tb: $LOD_{no\ gas} = 0.0004\ \mu g\ L^{-1}$, $LOD_{N2O} = 0.0004 \mu g\ L^{-1}$).

In general it is evident, that the N_2O mode with the exception of Sc, Ga, In and Te always features lower *LOD*s compared to the O_2 mode. Nevertheless, the *LOD*s for Sc, Ga and In in the N_2O mode (Sc: 0.010 $\mu g\ L^{-1}$, Ga: 0.04 $\mu g\ L^{-1}$ and In: 0.013 $\mu g\ L^{-1}$) lay within the same

range of their respective *LOD*s in the O_2 mode (Sc: 0.008 µg L^{-1}, Ga: 0.023 µg L^{-1} and In: 0.012 µg L^{-1}). Te shows a significantly higher *LOD* in the N_2O mode (0.13 µg L^{-1}) when compared to both other measuring modes which is caused by the ^{130}Xe interference on ^{130}Te. *LOD* may be improved by either using higher gas flows of N_2O or by with increasing energy discrimination voltage. Yet, all other analytes of interest exhibit better oxide formation rates or sensitivities for the parameters given in Table 1, hence the resulting inferior *LOD* of Te was a necessary compromise.

Overall, the best *LOD* improvements by using N_2O are achieved for Ge and Nb (Ge: 0.024 µg L^{-1} compared to 0.051 µg L^{-1} (no gas) and 0.045 µg L^{-1} (O_2 mode); Nb: 0.023 µg L^{-1} compared to 0.028 µg L^{-1} (O_2 mode)).

Table 4 lists measured elemental mass fractions of selected TCEs and recoveries for the analysis of three reference materials (GBW 07311, BCR-2 and GBW 07313). Recoveries of the developed method ranged between 72% to 106% for GBW 07311, 87% to 107% for BCR-2 and 69% to 112% for GBW 07313. Under consideration of the calculated uncertainties of the measurement, as well as given uncertainties of the reference materials, the determination of all analytes can be assumed accurate as long as recoveries range between 70% and 120%.

For Nb, the reference material GBW 07313 shows a recovery of only 69%. However, the given reference value does not feature any information regarding the exact uncertainty.

Recoveries of Te for the reference material GBW 07311 were significantly higher (185%) than certified. This is in accordance with Zimmermann *et al*. *(2020)*[17] who found a similar recovery rate, which the authors measured in single MS mode as ^{125}Te. Therefore, it can be assumed that the isobaric interference of ^{130}Ba on ^{130}Te does not explain the non-quantitative recovery. One explanation for the significantly higher recovery rate may be an carbon induced signal enhancement as described by *Grindlay et al*. (2013).[35] It is predicted that in presence of carbon some hard-to-ionize analytes like Sb, Te, Au, Se, As, Hg, I and P may experience a signal enhancement during ICP-MS measurements mainly induced by possible charge transfer reactions of C^+ or CO^+ ions.[35] The total carbon content of the reference material is about 0.24%, which may already lead to an enhanced Te signal. For further validation a multi-element in house standard[2] without additional carbon was measured and screened for Te (n = 12). For this

[2] This standard contains the Elements: Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, In, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, , Sb Se, Sn, Sr, Te, Ti, Tl, U, V, Zn, REE at either 25.00 µg L^{-1}, 250.0 µg L^{-1} or 2500 µg L^{-1}

standard Te showed a recovery of 94% ($m_{easurement}$ = 24 µg L^{-1} ± 6 µg L^{-1}, $c_{reference}$ = 25.0 µg L^{-1} ± 1.3 µg L^{-1}) indicating an accurate measurement.

To summarize, our results prove that all analytes give accurate and reproducible results using the presented method. It should be noted, that the development of multi-element methods often result in compromises with regard to e.g. *LOD*s or *LOQ*s as it is rarely possible to find the perfect method parameter for all analytes simultaneously. Therefore, potentially slightly better *LOD*s or *LOQ*s may be achieved in single-element analysis.

Table 3 LODs and of all measured elements in no gas, O_2 and N_2O mode. The respective elements were measured either in single MS (only Q1) mode or MS/MS mode (Q1 and Q2)

			single MS	**MS/MS O_2**	**MS/MS N_2O**
Analyte	**Q1**	**Q2**	***LOD* / µg L^{-1}**	***LOD*/ µg L^{-1}**	***LOD* / µg L^{-1}**
Sc	45	61	0.7	0.008	0.010
Ga	71	71	0.04	0.023	0.04
Ge	72	88	0.05	0.05	0.024
Y	89	105	0.02	0.019	0.017
Nb	93	125	0.012	0.0028	0.0023
In	115	115	0.016	0.012	0.013
Te	130	130	0.06	0.012	0.13
La	139	155	0.006	0.008	0.006
Ce	140	156	0.011	0.011	0.009
Pr	141	157	0.0010	0.0015	0.0013
Nd	146	162	0.004	0.004	0.0028
Sm	147	163	0.0008	0.0022	0.0011
Eu	153	169	0.0003	0.0006	0.00023
Gd	157	173	0.0015	0.0016	0.0014
Tb	159	175	0.0004	0.001	0.0004
Dy	163	179	0.0024	0.004	0.003
Ho	165	181	0.0006	0.0012	0.0006
Er	166	182	0.0021	0.0027	0.0023
Tm	169	185	0.0004	0.0012	0.00029
Yb	172	188	0.0026	0.004	0.0016
Lu	175	191	0.0006	0.0010	0.0004

Analyte	Q1	Q2	single MS *LOD* / µg L^{-1}	MS/MS O_2 *LOD*/ µg L^{-1}	MS/MS N_2O *LOD* / µg L^{-1}
Ta	181	197	0.0016	0.0027	0.0020

Table 4 Measured and certified mass fractions of the analyzed reference materials GBW 07311 (n=7), GBW 07313 (n=4) and BCR-2 (n=10). Errors correspond to expanded uncertainties (U, k=2). All italicized values are either information values provided on the certificates or from references 36, 35, and 38.[36-38]

	GBW 07311 (*n*=7)			BCR-2 (*n*=10)			GBW 07313 (*n*=4)		
Analyte	certified range / mg kg^{-1}	measured / mg kg^{-1}	recovery	certified range / mg kg^{-1}	measured / mg kg^{-1}	recovery	certified range / mg kg^{-1}	measured / mg kg^{-1}	recovery
Sc	7.4 ± 0.4	5 ± 3	72%	33 ± 2	29 ± 11	87%	25.6 ± 2.9	28.8 ± 2.4	112%
Ga	18.5 ± 0.9	20 ± 5	106%	23 ± 2	23 ± 4	100%	23.7 ± 1.7	22.2 ± 2.2	94%
Ge	1.81 ± 0.21	1.9 ± 0.7	103%	*1.46*[36] ± *0.26*[36]	1.48 ± 0.33	102%		2.12 0.23	
Y	43 ± 5	36 ± 9	82%	37 ± 2	35 ± 5	95%	104 ± 5	107 ± 13	103%
Nb	25.0 ± 3.0	25 ± 6	101%	*12.41*[36] ± *0.02*[36]	11.4 ± 1.9	91%	*15.1*	10.4 ± 1.1	69%
In	1.9 ± 0.3	1.8 ± 0.5	97%	*0.09127*[37] ± *0.00094*[37]	0.087 ± 0.016	95%		0.139 ± 0.017	
Te	0.4 ± 0.1	0.74 ± 0.19	185%	*0.004*[36]	< LOD	-		3.04 ± 0.28	
La	30 ± 2	30 ± 8	100%	25 ± 1	27 ± 4	107%	67.8 ± 2.9	68 ± 8	101%
Ce	58 ± 4	61 ± 13	105%	53 ± 2	55 ± 8	104%	92 ± 8	92 ± 11	100%
Pr	7.4 ± 0.5	7.3 ± 1.7	98%	6.8 ± 0.3	7.2 ± 1.4	105%	20.1 ± 1.9	20.6 ± 2.5	103%
Nd	27 ± 2	26 ± 7	98%	28 ± 2	30 ± 6	106%	92 ± 4	86 ± 8	94%
Sm	6.2 ± 0.3	6.0 ± 1.8	97%	6.7 ± 0.3	6.5 ± 1.2	98%	21.5 ± 1.3	18.5 ± 2.0	86%
Eu	0.6 ± 0.06	0.57 ± 0.16	94%	2.0 ± 0.1	1.9 ± 0.3	97%	5.3 ± 0.3	4.6 ± 0.6	86%
Gd	5.9 ± 0.4	5.7 ± 1.7	97%	6.8 ± 0.3	7.0 ± 1.2	102%	22.0 ± 1.2	20.3 ± 1.9	92%
Tb	1.13 ± 0.09	0.95 ± 0.28	84%	1.07 ± 0.04	1.02 ± 0.16	95%	3.4 ± 0.3	3.0 ± 0.4	87%
Dy	7.2 ± 0.6	6.1 ± 1.9	84%		6.4 ± 1.0	-	19.9 ± 1.8	18.1 ± 2.4	91%
Ho	1.4 ± 0.2	1.2 ± 0.37	85%	1.33 ± 0.06	1.26 ± 0.16	95%	4.3 ± 0.2	3.5 ± 0.5	81%

	GBW 07311 (*n*=7)		BCR-2 (*n*=10)		GBW 07313 (*n*=4)	
Analyte	certified range / mg kg^{-1}	measured / mg kg^{-1}	recovery	certified range / mg kg^{-1}	measured / mg kg^{-1}	recovery	certified range / mg kg^{-1}	measured / mg kg^{-1}	recovery
Er	4.6 ± 0.5	3.6 ± 1.1	78%		3.6 ± 0.5	-	11.0 ± 0.7	9.7 ± 1.2	88%
Tm	0.74 ± 0.09	0.57 ± 0.17	77%	0.54	0.50 ± 0.07	93%	1.54 ± 0.14	1.36 ± 0.20	89%
Yb	5.1 ± 0.6	3.9 ± 1.2	77%	3.5 ± 0.2	3.2 ± 0.5	92%	9.8 ± 1.1	8.8 ± 1.2	89%
Lu	0.78 ± 0.06	0.60 ± 0.21	77%	0.51 ± 0.02	0.51 ± 0.09	99%	1.46 ± 0.19	1.32 ± 0.16	91%
Ta	5.7 ± 0.5	5.0 ± 0.9	88%	*0.79*[a] ± *0.02*[a]	0.70 ± 0.21	89%	*1.11*[38] ± *0.13*[38]	0.81 ± 0.07	73%

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Conclusion

The developed approach of measuring TCEs in sediment digests by ICP-MS/MS using N_2O as a reaction gas allows the quasi-simultaneous and accurate analysis of Ga, Ge, Nb, In, Te, Ta as well as REEs. For at least one of the measured reference material, recoveries ranging from 80% to 112% could be achieved for all analytes. Additionally, *LOD*s and *LOQ*s of Ge, Y, Nb, Ce, Nd, Eu, Gd, Ho, Tm, Yb, and Lu were significantly improved by means of N_2O as a reaction gas, since possible interferences (e.g. Nd^{2+} or Sm^{2+}) can be effectively removed.

Consequently, the new method enables the determination of elemental mass fractions of TCEs in sediment samples, which can help to gain better insights into the behavior of these elements in the marine environment or to determine their origin, fate and distribution within complex land-river-sea systems. Validated analytical workflows are of great importance to understand the future role of TCEs as potential emerging inorganic contaminants. Furthermore, the N_2O gas mode may be easily implemented in already existing ICP-MS/MS multi-element methods to analyze not only TCEs/REEs, but other elements are also deemed to benefit from oxide formation such as Ti, Mo, or W. Therefore, we propose to replace O_2 by N_2O as standard oxidizing agent in ICP-MS/MS measurements, due to significantly higher oxide formation rates observed for many elements.

In a future applications in the frame of environmental studies, our method will be used to investigate the input of TCEs into the environment, with special emphasis on In and Ga inputs, from offshore wind farms in the German Bight, which play a key role in the ongoing energy transition in Germany to achieve the sustainable development goals of the United Nations. Therefore, the general background concentrations of the individual TCEs in the German Bight will be investigated as well as the extent to which offshore wind farms represent sources for TCEs affecting their surrounding environment.

Conflict of interest

The authors have no competing interests to declare.

Acknowledgment

The authors would like to thank Madita Kruse for her support in the laboratory.

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