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Paper

Development and application of an analyte/matrix separation procedure for multi-element trace analysis of steel alloys by means of sector-field ICP-mass spectrometry

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An analytical procedure, based on the use of sector-field ICP-mass spectrometry (ICP-SFMS), was developed for the determination of Be, B, Al, P, S, Ti, Ge, As, Se, Zr, Nb, Rh, Pd, Sn, Sb, Hf, Ta, W, Re, Ir and Pt in a high-alloy steel matrix, consisting mainly of Cr, Fe and Ni, in addition to lower amounts of Si, V, Mn, Co, Cu and Mo. To reduce the impact of spectral and non-spectral interferences, an analyte/matrix separation procedure based on cation-exchange chromatography was developed and applied. In the chromatographic protocol used, most of the first row transition metals are retained on AG 50Wx8 resin, whereby ca. 97.5 % of the initial matrix can be separated from the rapidly eluting target elements. The main matrix constituents accompanying the rapidly eluting target elements are Si, Mo and ca. 5 % of the total Cr, the latter of which unavoidably elutes prematurely. The finalised procedure was applied to CRMs and real high-alloy steel samples (T91, 316L and 15-15Ti). The experimentally determined concentrations for the CRMs were found to be in good agreement with certified values. Analysis of the real samples revealed the presence of measureable amounts of most of the target elements in at least one of the three steels, with the exception of Be, S, Se, Hf and Ir. For elements not natively found in the CRMs or the real samples under study, recoveries of 100 % (within reproducibility uncertainty) were obtained when analysing mock samples. Procedural limits of quantification (10 *s* LoQs) were determined by subjecting blanks to the entire procedure. These were found to range from low ng/g levels for Re to sub-mg/g levels for S.

1 Introduction

The Belgian Nuclear Research Centre SCK●CEN has been developing a multi-purpose accelerator-driven system (ADS) for various R&D applications since the 1990s. Once operational, this multi-purpose hybrid research reactor for high-tech applications (MYRRHA) will serve as a source of protons and neutrons for a variety of R&D applications. The interested reader is referred to Abderrahim *et al.* for a detailed description of MYRRHA's current design, as well as the reactor's task profile.[1] This research reactor will use a high power proton accelerator to bombard a liquid lead-bismuth eutectic (LBE) spallation target, which, in turn, is coupled to an LBE-cooled subcritical fast core.[1–4]

The innovative nature of this nuclear reactor design poses new challenges with regard to structural material performance. The austenitic stainless steels 316L and 15-15Ti have been well characterised for use as structural materials in nuclear installations such as sodium cooled fast reactors (SFR). The ferritic-martensitic steel T91 is a relatively new structural material for nuclear reactors, but it has better creep resistance, better swelling resistance and a higher thermal strength than austenitic steels. However, conditions within the MYRRHA reactor will be harsher than in existing installations. Although LBE has been considered as a primary coolant due to its excellent neutronic and thermodynamic properties, the heavy liquid metal (HLM) coolant is highly corrosive under certain conditions and may also affect a steel's mechanical characteristics. In addition, the envisaged operating temperature range for MYRRHA is lower than for an SFR and some of its components will be exposed to both proton and neutron irradiation. Nonetheless, currently available and already qualified industrial steels (T91, 316L and 15-15Ti) are being considered for use as structural or fuel cladding materials, rather than developing innovative materials. The austenitic stainless steel 15-15Ti has been selected as fuel cladding material, whilst the ferritic-martensitic steel T91 has been selected for the wrapper of the fuel assembly, the core support plate and the spallation target window. For most other major components, such as the reactor vessel and the heat exchangers, the austenitic stainless steel 316L has been selected. These three existing materials were chosen, in part, because MYRRHA is intended to be fully operational within less than a decade and because it was anticipated that these particular steels would exhibit some resistance to the aforementioned issues.[5–7]

Trace and minor elements in such alloys may improve or deteriorate a steel's mechanical characteristics, such as hardness[8]. In addition, radiotoxic nuclides may be produced by activation of trace, minor or matrix elements present in both the reactor steels[9] and the LBE coolant[10]. Contamination of the structural materials or the coolant, due to neutron radiation, could have implications with regard to reactor decommissioning. Accurate and precise determination of a number of trace and minor elements is therefore of importance, both in the coolant and in several types of steels. In a previous paper, the authors examined the situation from the perspective of the coolant, and reported an analytical procedure for the determination of a large number of trace elements in an LBE matrix[11]. In this study, the authors focused on the structural materials to develop an analytical procedure for the determination of trace elements in high-alloy steels. Impurities and alloying elements that are expected to be present in the three steel alloys in question include B, Al, Si, P, S, Ti, V, Mn, Co, Cu, As, Zr, Nb, Mo, Ta and W in addition to the main matrix elements Cr, Fe and Ni.

Double-focusing sector-field inductively coupled plasma-mass spectrometry (ICP-SFMS) is a highly sensitive element-selective analytical technique, which can be used for the determination of a large number of trace elements in steel alloys. However, the accurate and precise determination of trace elements may be hampered by spectral and non-spectral interferences. Although many spectral interferences can be easily resolved by operating the ICP-SFMS instrument at higher mass resolution, non-spectral interferences are more difficult to predict and to correct for. These issues are discussed in a number of texts that describe the operating principles, important considerations and applications of this technique[12–15].

In the specific case of digested high-alloy steels, the occurrence of spectral interferences, originating mainly from the matrix elements present at levels > 5 %[16], has been reported. All three of the alloys under consideration contain > 5 % Cr, whilst both 316L and 15-15Ti also contain > 5 % Ni. Therefore, Cr-, Fe- and Ni-based polyatomic interferences may be formed at appreciable levels when analysing such samples. One strategy to eliminate these spectral interferences, whilst simultaneously reducing matrix effects, is to selectively isolate the trace elements from the matrix elements. In the past, macro-quantities of Fe have been separated from a number of other elements, *e.g.*, by using anion-exchange chromatography[17]. However, it is impossible to also remove Cr and Ni by using this particular technique. The determination of trace B in high-alloy steels has, *e.g.*, also been achieved by a combination of matrix precipitation and cation-exchange chromatography[18]. Although in this case, whilst matrix removal was highly efficient, the recovery of B was < 40 % and isotope dilution ICP-MS had to be applied. Naturally, the latter would be impractical for the determination of a large number of trace elements in a large number of samples. In this work, we have therefore attempted to develop a procedure based solely on the use of cation-exchange chromatography.

Although Nelson *et al.* studied the affinity of a large number of elements for the AG 50x4 cation exchange resin in HCl media[19] extensively, data on their affinity for similar resins in HNO_3 or HF media is much sparser[20, 21]. Nonetheless, from the data available, it can be concluded that Cr, Fe and Ni ought to be retained on the resin in dilute HNO_3/HF media. At the same time, a large number of the alloying elements and impurities should exhibit little or no affinity for the resin in these types of media.

The initial aim of this work was to develop an analytical method for the determination of trace levels of B, Al, P, S, Ti, As, Nb, Zr, Ta and W in the high-alloy steels T91, 316L and 15-15Ti. To allow for the accurate determination of these target elements, by means of ICP-SFMS, spectral and non-spectral interferences have to be dealt with. To this end, the use of a chromatographic analyte/matrix separation procedure was considered. Highly selective chromatographic resins are commonly used to isolate a single target element from a difficult matrix. However, in this case, selectively retaining the three main matrix elements on an AG 50Wx8 cation-exchange resin, whilst rapidly eluting the trace elements of interest, was deemed to be an appropriate approach. In addition, the applicability of the procedure has been extended beyond the initial set of target elements as also the determination of the additional elements (Be, Ge, Se, Rh, Pd, Sn, Sb, Hf, Re, Ir and Pt) in these high-alloy steels was deemed possible.

2 Experimental

2.1 Instrumentation

Quantitative measurements were performed using an Element 2 ICP-SFMS instrument (Thermo Scientific, Germany), modified for use with a nuclear glovebox. This instrument's sample introduction system consists of a PFA-ST self-aspirating nebuliser (Elemental Scientific, Omaha, USA), an inert PFA double-pass Scott-type spray chamber (Savillex, USA), a demountable quartz torch and injector (Thermo Scientific, Germany), and a SC-2 FAST autosampler (Elemental Scientific, USA). The sample line and internal standard line are both pumped using a multi-channel peristaltic pump (Perimax, Spetec, Germany) and the two flows are mixed online in a 1:1 ratio, by means of a T-piece (Elemental Scientific, USA), which is positioned just before the nebulizer. Li, Sc, Ga, Sr, In, Eu and Th were used as internal standards, because they cover the greater part of the mass range[22]. In the case of the target elements, two of the most abundant nuclides, free from isobaric interference, were monitored whenever possible. Generally speaking, the most abundant nuclide was most often used for quantitative purposes. Typical instrument settings are summarized in Table 1. The instrument was tuned daily for maximum sensitivity and stability to count rates of ≥ 1×10^5, 1×10^6, and 1×10^6 counts/s per µg/L for $^{7}Li^+$, $^{115}In^+$ and $^{238}U^+$, respectively, prior to starting a measurement sequence. Essentially, this amounted to optimising the nebulizer flow rate and the torch position on a daily basis. Mass calibration for the instrument's medium and high resolution modes was also carried out on a daily basis. In addition, the accuracy of the mass calibration was verified throughout each measurement sequence by monitoring the mass spectra. If necessary, the relevant mass offsets were adjusted as required in the Element software. The nuclides of Be, B, Zr, Nb, Mo, Rh, Pd, Sn, Sb, Hf, Ta, W, Re, Ir, Pt were measured in low resolution mode, whilst those of Al, Si, P, S, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and those of Ge, As, Se were measured in medium and high resolution modes, respectively. Low, medium and high resolution measurements were carried out in separate measurement sequences (often on different days). Calibration standards and dilutions were prepared such that the instrument's detector always operated in the pulse counting mode for all nuclides monitored.

2.2 Reagents and labware

Trace metal grade HNO_3 (67 - 69 wt.%), HF (47 - 51 wt.%) and HCl (34 - 37 wt.%) were obtained from Fisher Scientific (Belgium). These *trace metal grade* acids and ultrapure (UP) water with a resistivity of ≥ 18.2 MΩ·cm (Arium Pro UV, Sartorius Stedim Biotech, Belgium) were used throughout to prepare samples, eluents, standards and dilutions. Standard solutions were prepared by gravimetric serial dilution of commercially available single-element stock solutions (1 g/L). These stock solutions were obtained from CPI (The Netherlands), Johnson Matthey (UK) and, in the case of Spex Certiprep (UK) solutions, from Boom BV (The Netherlands). Multi-element stock solutions (Spex Certiprep, 10 mg/L) were used to verify calibration curves, and for preparing "synthetic" and "mock" samples (See section 2.3).

Three steel alloy CRMs were obtained from the National Institute of Standards and Technology (MD, USA) in the form of chips (NIST SRMs 361, 362 and 363). Actual T91 and 316L samples were obtained from Industeel (Belgium), whilst a 15-15Ti sample was obtained from OCAS (Belgium).

Dry AG 50Wx8 cation-exchange resin (100-200 mesh) and 5 mL polypropylene columns were obtained from Triskem International (France). The AG 50Wx8 resin was rinsed with UP water and stored in a 0.25 M HCl medium. The columns, in turn, were rinsed with UP water and stored in a 1.5 M HNO_3 medium. Both the resin and the columns were stored in these dilute acids for at least one week prior to use. On the actual day of use, the resin was rinsed first with UP water and then with the initial eluent to be used during the separation procedure. The resin slurry was then loaded into the column, which had also been rinsed with UP water prior to use. The loaded column was finally conditioned with 10 mL of the initial eluent.

All labware was made of HDPE, PP or PTFE and was cleaned by leaching with 1.5 M HNO_3 for at least 48 h. Sealable PTFE digestion vessels (Savillex, USA) were cleaned by leaching with 3 M HNO_3 and 2.4 M HCl at ca. 175 °C on a hotplate.

Argon gas (> 99.999%), used to operate the ICP-SFMS instrument was obtained from Air Products (Belgium).

A 4 mm diameter titanium coated metal drill bit (Bosch, Germany) was used to collect steel alloy samples.

2.3 Sample preparation procedure

Simple "synthetic" samples were prepared by serial dilution of multi-element and single-element (in the case of Fe) stock solutions in such a way that they contained 2 mg/L Fe and 0.2 mg/L of each other element.

Real samples were prepared by digesting the high-alloy steel. The high-alloy steel was first drilled with a metal bit to a depth of ca. 2 to 3 mm, whereafter the material originating from this surface layer was collected and discarded (in order to remove potential surface contaminants). The same metal drill bit was then used to drill further down into the sample, after which the drillings of the sub-surface layers were collected for quantitative analysis. For digestion, ca. 0.5 g metal was weighed in a sealable PTFE digestion vessel. A 2.5 mL aliquot of HCl was pipetted into this vessel, followed by a 2.5 mL aliquot of HNO_3 and 0.25 mL of HF. The vessel was then closed and placed on a hotplate at 175 °C for 8 h, after which it was left to cool before opening. The bulk of the material had usually dissolved at this stage, although the solution was most often not yet clear. Therefore, a 1.75 mL aliquot of UP water was pipetted into the vessel, after which it was closed and placed on a hotplate at 200 °C for another 8 h. After cooling, ca. 18 mL of UP water was pipetted into this vessel, bringing the total volume to ca. 25 mL. The sample solution then contained at most 20 000 mg/L Fe and acids at concentrations of at most 1.5 M HNO_3, 1.2 M HCl and 0.3 M HF.

"Mock" samples were prepared by digesting drillings, as described in the previous paragraph (mock samples prepared for validation purposes were all prepared from T91 steel drillings). A 4.4 mL aliquot of the resulting solution was taken and spiked with 0.2 mL of three 10 mg/L multi-element stock solutions. The amount of spike added would be equivalent to ca. 20 µg/g of each of the target elements in the original solid material.

Certified reference materials, obtained in the form of chips, were digested in the same way as drillings from real samples.

Procedural blank samples were also prepared in the same manner, except that no actual solid material was digested.

Table 1 Element 2 Instrument settings and parameters

Setting/parameter	Value/Description		
Autosampler	ESI SC-2 Fast		
Internal standards	Li, Sc, Ga, Sr, In, Eu and Th		
Aspiration mode	Pumped (2 x ~125 µL/min)		
Nebuliser	PFA-ST		
Spray chamber	Inert PFA double-pass Scott-type		
Torch and injector	Demountable/Quartz		
Sampling cone	Ni (1.0 mm aperture diameter)		
Skimmer cone	Ni (H-type, 0.8 mm aperture diameter)		
Plasma/Cool gas	~16 L/min		
Auxiliary gas	~0.8 L/min		
Sample gas*	1.00 – 1.10 L/min		
Guard electrode	Enabled		
RF Power	~1250 W		
Scan type	E-Scan		
Detector mode	Dual		
Resolution (m/Δm)	~300	~4000	~10 000
Runs	6	6	6
Passes	12	6	6
Dwell time	10 ms	20 ms	20 ms
Mass Window	5 %	100 %	125 %
Integration window	5 %	60 %	60 %
Samples per peak	100	20	20
Elements	Li, Be, B, Sc, Ga, Sr, Zr, Nb, Rh, Pd, In, Sn, Sb, Eu, Hf, Ta, W, Re, Ir, Pt, Th	Al, Si, P, S, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ga, Mo	Sc, Ga, Ge, As, Se, Sr

** Optimised on a daily basis for maximum $^{7}Li^{+}$, $^{115}In^{+}$ and $^{238}U^{+}$ signal intensities and optimum stability*

3 Results and discussion

3.1 Analyte/matrix separation procedure

The analyte/matrix separation procedure developed in this work relies on the use of a cation-exchange resin. The AG 50Wx8 resin has a high affinity for the matrix elements Cr, Fe and Ni in dilute HNO_3 media, whilst it should exhibit little to no affinity for many of the target elements in the same dilute HNO_3 media.

The affinity of the following elements B, Al, P, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, As, Mo, Zr, Nb, Ta and W for the AG 50Wx8 resin in acidic media (dilute HNO_3, HCl, HF) was investigated. The behaviour of all these elements was studied by loading a 1 mL aliquot of a synthetic sample onto a 5 mL AG 50Wx8 column. Such samples were then eluted using a variety of eluents with varying HNO_3 (0.15 M, 0.3 M, 0.75 M, 1.5 M, 3 M, 4.5 M), HCl (0 M, 0.12 M, 0.24 M, 0.6 M, 1.2 M) and HF (0.003 M, 0.012 M, 0.3 M) concentrations. Based on these experimental data, the separation procedure was optimised in terms of the acids' concentrations in the eluent. In essence, the HNO_3 concentration in the eluent needs to be sufficiently low to ensure retention of Cr, Fe and Ni, as was expected, whilst the HF concentration needs to be high enough to ensure rapid elution of Al, Ti, Zr, Nb and W. As an example of matrix element behaviour, Figure 1(a) depicts elution profiles of Ni for a range of HNO_3 concentrations, at a constant 0.012 M HF concentration. This shows that Ni is fully retained on the resin at molarities ≤ 1.5 M, while the affinity is expected to be highest at 0.15 M HNO_3. As an example of target element behaviour, Figure 2(a) depicts elution profiles of Zr for the same range of HNO_3 concentrations, showing that Zr is rapidly eluted from the resin at all molarities studied. Figure 2(b) depicts elution profiles of Zr for a range of HF concentrations, at a constant 0.3 M HNO_3 concentration. Although these elution profiles show that 0.012 M HF in the eluent ensured rapid elution of Zr, a 0.3 M HF concentration was found to be required to rapidly elute every single target element prone to form fluoride complexes (*e.g.,* Al, Ti and Nb). Rapid elution of the target elements ensures good separation from the matrix elements, if the latter are strongly bound to the resin under the same conditions. Figure 1(b) reveals that HF concentrations of up to 0.3 M do not impede retention of the matrix element Ni on the AG 50Wx8 resin, and a similar observation was made for the two other matrix elements, Cr and Fe. Whilst the use of HCl was found to be essential for the actual digestion of real high-alloy steel samples, it was feared that the presence of this HCl in the digested samples might still reduce the resin's affinity for a matrix element such as Fe. However, as shown in Figure 1(c) and Figure 2(c), the presence of HCl at concentrations up to 1.2 M in the eluent did not affect elution behaviour adversely. Generally speaking, when using a 0.15 M HNO_3 / 0.3 M HF eluent, the elements V, Cr, Mn, Fe, Co, Ni and Cu have a high affinity for the AG 50Wx8 resin; whilst B, Al, P, Ti, As, Zr, Nb, Mo, Ta and W are rapidly eluted. The elements initially retained on the column can then be stripped with a 7.5 M HNO_3 / 0.3 M HF eluent for their separate determination.

The analyte/matrix separation procedure was then applied to mock samples, with much higher concentrations of the matrix elements compared to the synthetic samples. Experiments with these mock samples revealed that the procedure can also be used for the determination of Be, S, Ge, Se, Rh, Pd, Sn, Sb, Hf, Re, Ir and Pt. The procedure was applied to mock samples originating from the three types of high-alloy steels T91, 316L and 15-15Ti, from which three elution profiles were constructed for each element. The intra-element similarity of these elution profiles was testament to the reproducibility of the procedure.

In the optimised procedure, a 1 mL sample, containing ca. 10 000 to 20 000 mg/L Fe and at most 1.5 M HNO_3, 1.2 M HCl and 0.3 M HF, is loaded onto the 5 mL AG 50Wx8 column. Most of the trace elements and minor elements are easily stripped from the column by eluting with 9 mL of a 0.15 M HNO_3 / 0.3 M HF eluent (Fraction T). The remaining elements V, Cr, Mn, Fe, Co, Ni and Cu are eluted using 30 mL of a 7.5 M HNO_3 / 0.3 M HF eluent (Fraction M). Examples of elution profiles, for all of the elements considered in this work, obtained by applying the analyte/matrix separation procedure to a mock sample, are presented in Figure 3.

Approximately 5 % of the Cr present in a high-alloy steel, i.e. < 1 % of the initial matrix, elutes prematurely and ends up in the first fraction (Fraction T) containing the target elements. In a separate experiment, it was found that the speciation of Cr changes whilst a sample solution undergoes heating, with prolonged heating resulting in an increase in the amount of Cr that breaks through. However, this issue was not investigated further. The minor element Mo, constituting ca. 1 - 2 % of the total of each steel alloy matrix, also co-elutes with the target elements. Given that the amount of Mo ending up with the target elements exceeds that of prematurely eluting Cr, no further effort was made to reduce the amount of Cr that breaks through. In the case of Fe and Ni, in contrast to Cr, > 99.9 % of both of these matrix elements could be separated from the target elements. However, in an additional experiment, it was found that as much as ~10 % of Fe could elute from the AG 50Wx8 column prematurely if the HCl concentration in the digested sample was doubled to 2.4 M instead of being limited to 1.2 M.

3.2 Validation of the procedure

Validation of the procedure was carried out by analysing three types of samples. Firstly, the procedure was applied to three steel matrix CRMs (NIST SRMs 361, 362 and 363). Secondly, to evaluate the procedure for the determination of elements not natively found in the CRMs or real samples under study, the procedure was also applied to one type of mock sample (prepared from T91 steel). Thirdly, the procedure was applied to three real high-alloy steel samples (T91, 316L and 15-15Ti steel). Procedural limits-of-quantitation (LoQ, 10 *s*) were determined by analysing five procedural blanks. The procedural LoQs for all the trace and minor elements found in fraction T are presented in Table 2. These were calculated as if the procedural blank signal originated from a 0.5 g metal sample. These LoQs range from low ng/g levels for Re and Hf to sub-mg/g levels for S. All analyses of samples for validation purposes were carried out in quintuplicate (n = 5) under reproducibility conditions. For each replicate analysis, separate aliquots of any particular solid sample were digested on different days. ICP-SFMS measurements for each of the replicates were also carried out on separate days using different calibration standards.

The certified values and information values (in brackets) of the three CRMs are presented in Table 3, along with the experimentally determined concentrations for the target elements recovered in fraction T. For those target elements for which the concentrations in the three CRMs are certified, the experimentally determined concentrations were generally found to be in good agreement with their certified values. Recoveries of B, Al, Ti, As, Zr, Nb, Sn, Sb, Ta and W ranged from 93 % to 107 % for NIST SRM 361, whilst they lay between 83 % and 119 % for NIST SRM 362. In the case of NIST SRM 363, recoveries of 92 % to 104 % were obtained for B, Al, Ti, As, Zr, Nb, Sn and W; excluding a value of ca. 80 % for Sb (because the relative uncertainty associated with the certified value was 50 %). Recoveries of P were consistently low for all three CRMs (ca. 85 %), whilst the attainable procedural LoD for S was found to be too high to draw any conclusions. Unravelling the reason behind the inadequate recovery of P (*e.g.* loss of volatile species during digestion) was assessed to be beyond the scope of the current study by the authors. Information values available for Se were also in good agreement with experimental values for two out of the three CRMs, whilst experimental values for Ge and Hf were found to be considerably lower than their respective information values. However, adequate recoveries (see next paragraph) were obtained for both Ge and Hf when analysing mock samples.

Recoveries of target elements from mock samples, prepared by spiking dissolved T91 steel with multi-element stock solutions, were around 100 %, within the reproducibility uncertainty ($k = 2$). Recoveries, for those target elements found to be present in T91 steel at concentrations < 10 µg/g, are presented in Table 4. These ranged from 98 % for B to 106 % for Zr. Most importantly, excellent recoveries were also obtained for both Ge (102 %) and Hf (99 %), which had not been the case for the three CRMs.

Finally, samples of the three real high-alloy steel types under consideration (T91, 316L and 15-15Ti) were subjected to the optimised procedure. Experimentally determined concentrations of all trace and minor elements recovered from fraction T are presented in Table 5, while values for minor and matrix elements recovered from fraction M are presented in Table 6 (the latter purely for information purposes). None of these high-alloy steel samples (T91, 316L and 15-15Ti) were found to contain measurable levels of Be, S, Se, Hf or Ir.

Conclusions and outlook

A quick and efficient analyte/matrix separation procedure, facilitating the determination of a large number of target elements in a high-alloy steel matrix, has been successfully developed. The matrix elements Cr, Fe and Ni are retained on an AG 50Wx8 cation exchange resin, whilst the target elements elute rapidly. With the proposed procedure, Be, B, Al, Si, P, S, Ti, Ge, As, Se, Zr, Nb, Mo, Rh, Pd, Sn, Sb, Hf, Ta, W, Re, Ir and Pt can be isolated from the matrix elements Cr, Fe and Ni. In the case of Fe and Ni, matrix separation efficiency is > 99.9 %, whilst for Cr it is limited to > 90 %. Overall, about 97.5 % of the total matrix could be separated from the target elements for the three high-alloy steels under consideration (T91, 316L, 15-15Ti).

The optimised procedure was validated by analysing (i) steel alloy CRMs, (ii) mock samples and (iii) real samples. Experimental results were in good agreement with certified values for three CRMs, whilst spike recoveries were ~100 % when analysing mock samples. Procedural LoQs (10 s) were determined by analysing procedural blanks. Finally, the procedure developed was applied to real steel alloy samples.

The procedure developed in this work was specifically aimed at the analysis of T91, 316L and 15-15Ti high-alloy steels. Self-evidently, however, the procedure can also be applied to other types of alloys or even other types of samples, such as iron meteorites or high-purity Fe and Ni.

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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

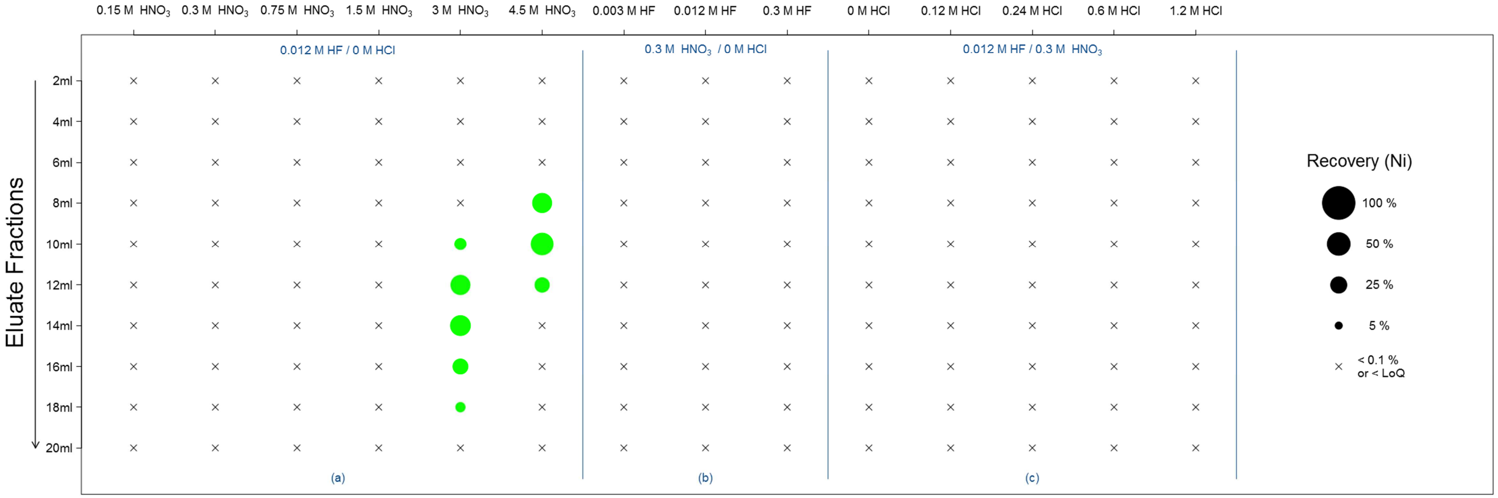


Figure 1 Isocratic elution profiles of Ni obtained upon loading 1 mL of a synthetic sample, containing ca. 0.2 mg/L Ni, on a 5 mL AG 50Wx8 column. For each of the different eluents investigated, the elution profile is represented as a series of circles, the areas of which are proportional to the recovery of an element in each respective fraction.

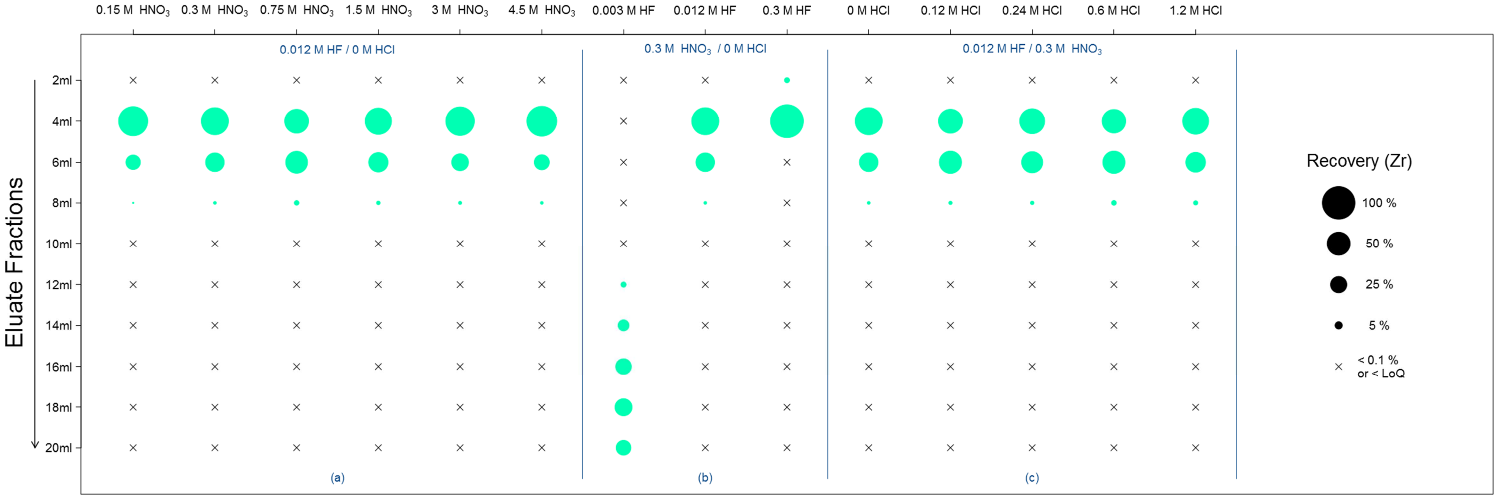


Figure 2 Isocratic elution profiles of Zr obtained upon loading 1 mL of a synthetic sample, containing ca. 0.2 mg/L Zr, on a 5 mL AG 50Wx8 column. For each of the different eluents investigated, the elution profile is represented as a series of circles, the areas of which are proportional to the recovery of an element in each respective fraction.

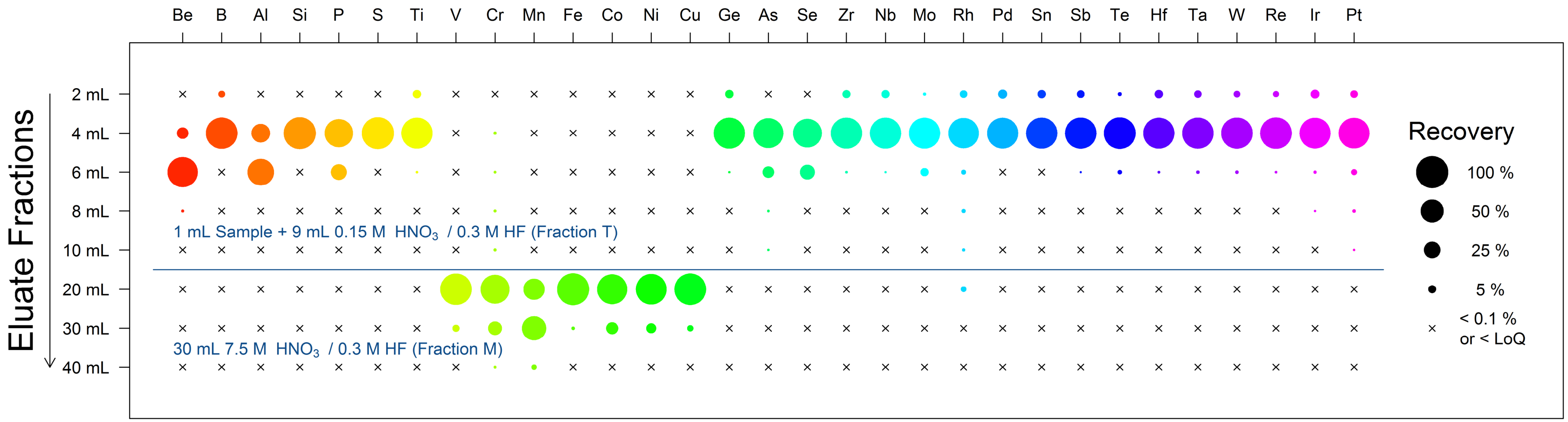


Figure 3 Gradient elution profiles for all elements of interest, obtained by applying the developed procedure to a mock sample prepared from 15-15Ti high-alloy steel. This mock sample was prepared such that it contained 10 000 – 20 000 mg/L Fe and at most 1.5 M HNO_3, 1.2 M HCl and 0.3 M HF. For each element, the elution profile is represented as a series of circles, the areas of which are proportional to the recovery in each respective fraction. The eluent used corresponds to the fractions collected as follows: [2 mL] 1 mL Sample + 1 mL 0.15 M HNO_3 / 0.3 M HF; [4 mL – 10 mL] 4 x 2 mL 0.15 M HNO_3 / 0.3 M HF; [20 mL – 40 mL] 3 x 10 mL 7.5 M HNO_3 / 0.3 M HF.

Table 2 Procedural limits-of-quantitation (LoQ, 10 *s*) for all the trace and minor elements that elute in fraction T.

	Be	B	Al	Si	P	S	Ti	Ge	As	Se	Zr	Nb
LoQ (µg/g)	0.2	1	20	900	7	200	0.4	0.2	0.1	0.5	0.1	0.02
	Mo	Rh	Pd	Sn	Sb	Te	Hf	Ta	W	Re	Ir	Pt
	4	0.01	0.1	0.4	0.02	0.06	0.007	0.02	0.03	0.005	0.8	0.2

Table 3 Experimental results and certified values for all target elements that elute in fraction T, for NIST SRMs 361, 362 and 363. The uncertainties on the experimentally determined concentrations have been rounded to two significant figures whilst the associated average values have been rounded to be in accordance.

SRM 361 (µg/g)	B	Al	P	S	Ti	Ge	As	Se	Zr	Nb	Sn	Sb	Hf	Ta	W
Experimental (*n*=5, *u*=2xSE)	4.80 ± 0.16	200.0 ± 4.1	121.0 ± 1.7	< 200	205.0 ± 2.8	33.80 ± 0.86	182.0 ± 3.2	32.40 ± 0.79	94.0 ± 5.1	210 ± 12	93.0 ± 4.3	42.0 ± 1.8	0.3240 ± 0.0087	196.0 ± 7.0	179.0 ± 4.9
Certified (*k*=2)	4.78 ± 0.15	210 ± 50	140 ± 10	143.0 ± 3.0	200 ± 10	-	170 ± 10	(40)	90 ± 10	220 ± 10	100 ± 10	42.0 ± 1.0	(2)	200 ± 10	170 ± 10
SRM 362 (µg/g)	B	Al	P	S	Ti	Ge	As	Se	Zr	Nb	Sn	Sb	Hf	Ta	W
Experimental (*n*=5, *u*=2xSE)	26.30 ± 0.63	790 ± 14	339.0 ± 9.0	320 ± 40	1000 ± 42	9.80 ± 0.31	840 ± 33	11.50 ± 0.51	2060 ± 72	3000 ± 120	182.0 ± 8.5	112.0 ± 5.9	0.530 ± 0.023	1980 ± 67	2250 ± 71
Certified (*k*=2)	25.0 ± 1.0	950 ± 50	410 ± 10	360.0 ± 3.0	840 ± 10	(20)	920 ± 50	(12)	1900 ± 100	2900 ± 100	160 ± 10	130 ± 10	(3)	2000 ± 100	2000 ± 100
SRM 363 (µg/g)	B	Al	P	S	Ti	Ge	As	Se	Zr	Nb	Sn	Sb	Hf	Ta	W
Experimental (*n*=5, *u*=2xSE)	12.60 ± 0.72	2440 ± 67	244.0 ± 5.4	< 200	520 ± 39	30.0 ± 2.2	92.0 ± 4.3	1.90 ± 0.29	460 ± 35	490 ± 39	990 ± 87	16.0 ± 1.4	0.960 ± 0.071	510 ± 36	480 ± 31
Certified (*k*=2)	13.10 ± 0.37	2400 ± 100	290 ± 50	68.0 ± 1.0	500 ± 10	(100)	100 ± 10	(2)	490 ± 10	490 ± 10	1040 ± 50	20 ± 10	(5)	(530)	460 ± 10

Table 4 Recoveries for target elements, obtained by applying the developed analyte/matrix separation procedure to a mock sample prepared from T91 steel. The recoveries of the target elements are expressed as percentages of the amount of spike, added (from multi-element stock solutions) to the dissolved samples, that was recovered. Only those elements for which the initial concentration in T91 steel was found to be < 10 µg/g are presented (amount of spike added is equivalent to 20 µg/g).

Recovery (%)	Be	B	Ge	Se	Zr	Rh	Pd	Sb	Hf	Ta	Re	Ir	Pt
Spiked T91 (*n*=5, *u*=2xSE)	102.4% ± 1.5%	98.1% ± 5.0%	101.8% ± 6.7%	100.1% ± 5.1%	105.5% ± 7.0%	104.8% ± 7.6%	98.5% ± 6.7%	100.4% ± 8.1%	98.9% ± 4.6%	98.6% ± 5.1%	99.6% ± 5.4%	104.3% ± 5.6%	99.0% ± 5.4%

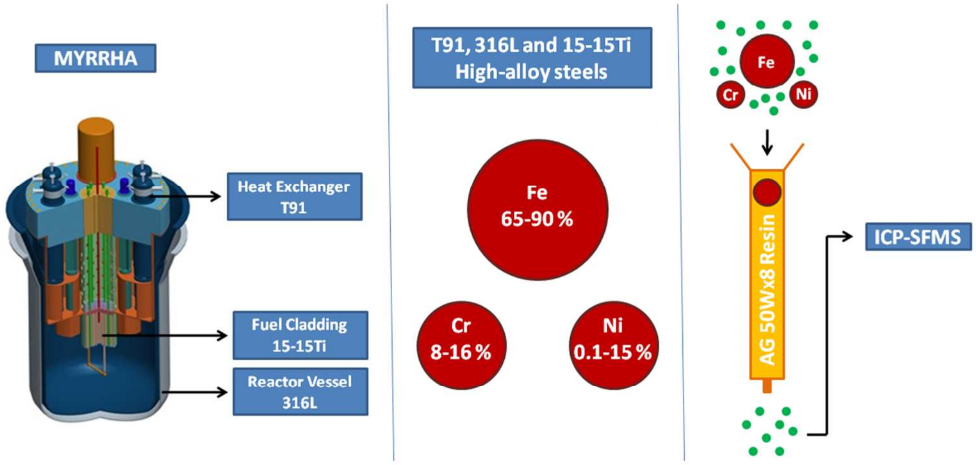
Table 5 Experimentally determined concentrations of trace and minor elements, found in fraction T, in three types of steel alloys (T91, 316L and 15-15Ti). The concentrations of Be, S, Se, Hf and Ir were found to lie below the procedural LoQ in all samples and have therefore not been reported in this table.

Conc. (µg/g) (*n*=5, *u*=2xSE)	B	Al	Si	P	Ti	Ge	As	Zr	Nb	Mo	Rh	Pd	Sn	Sb	Ta	W	Re	Pt
T91	1.09 ± 0.11	50.9 ± 2.3	2132 ± 84	178.0 ± 3.9	14.3 ± 1.1	6.57 ± 0.20	44.57 ± 0.65	< 0.1	691 ± 26	8560 ± 170	0.0128 ± 0.0041	< 0.1	30.52 ± 0.70	7.62 ± 0.20	0.811 ± 0.060	20.14 ± 0.51	1.235 ± 0.021	< 0.2
316L	15.48 ± 0.14	< 20	6750 ± 290	230 ± 10	9.70 ± 0.35	6.67 ± 0.15	70.50 ± 0.89	0.1163 ± 0.0099	6.10 ± 0.29	20160 ± 240	0.0717 ± 0.0091	< 0.1	80.1 ± 2.2	17.51 ± 0.41	0.034 ± 0.019	175.5 ± 2.5	1.276 ± 0.023	0.207 ± 0.014
15-15Ti	45.1 ± 1.2	169.3 ± 4.3	5830 ± 200	95.3 ± 3.1	4110 ± 110	2.295 ± 0.042	11.80 ± 0.15	0.111 ± 0.022	25.2 ± 1.3	12040 ± 220	0.029 ± 0.011	0.125 ± 0.012	5.40 ± 0.18	2.026 ± 0.066	0.1502 ± 0.0074	11.1 ± 1.1	0.619 ± 0.012	< 0.2

Table 6 Experimentally determined concentrations of minor and matrix elements, found in fraction M, in three types of steel alloys (T91, 316L and 15-15Ti).

Conc. (µg/g) (*n*=5, *u*=2xSE)	V	Cr	Mn	Fe	Co	Ni	Cu
T91	2033 ± 21	86580 ± 660	3736 ± 62	897000 ± 17000	109.9 ± 2.2	1165 ± 28	583.4 ± 2.4
316L	599 ± 15	164100 ± 1200	18280 ± 320	684000 ± 13000	602.1 ± 8.7	97200 ± 2900	2155 ± 30
15-15Ti	359.2 ± 8.0	149000 ± 1100	19120 ± 240	659000 ± 11000	190 ± 11	145600 ± 3700	227 ± 11

On the determination of trace elements in three high-alloy steels (T91, 316L and 15-15Ti), which are to be used as structural materials in a novel nuclear research reactor.


MYRRHA
Heat Exchanger T91
Fuel Cladding 15-15Ti
Reactor Vessel 316L
T91, 316L and 15-15Ti High-alloy steels
Fe 65-90 %
Cr 8-16 %
Ni 0.1-15 %
Fe
Cr
Ni
AG 50Wx8 Resin
ICP-SFMS