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Determination of Helium in Samples from the Irradiated Fuel Channel Spacers of CANDU Power Reactors by Vacuum Fusion-Mass Spectrometry

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Research Article

Keywords: Determination of transmuted helium

Posted Date: November 3rd, 2026

DOI: https://doi.org/10.21203/rs.3.rs-11380903/v1

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Additional Declarations: No competing interests reported.

Abstract

Nickel-based alloys have been important component materials for today's various types of nuclear power reactors and probably will continue to be in the future; however, neutron radiation can affect the mechanical properties and microstructure of the alloys causing damage to the materials through direct displacement of atoms and void swelling by gas generation from nuclide transmutations. Therefore, detailed understanding about neutron radiation damage through these mechanisms to nickel-based alloys is highly important to better assess the reactor component lifetime. Development of analytical methods capable of accurately measuring the helium content in irradiated and highly radioactive nickel alloy materials is essential for this purpose. This paper describes a vacuum fusion – mass spectrometry (VF-MS) method for determination of helium in irradiated nickel alloys. Based on the helium content and the radioactivity of the materials, helium concentrations of samples as small as 0.003 g have been determined accurately and precisely using this method. Up to 12 samples have been analyzed in one batch of analysis within the safe limits of radiation protection. Key experimental parameters, including fusion flux, fusion time and temperature, and mass spectrometric quantification techniques have been optimized. The VF-MS method was validated by analysing a quality control material and comparing the results with an independent laboratory using a different method, and with the predicted values. This method has been used to analyze specimens obtained from the ex-service fuel channel spacers in CANDU® nuclear reactors. The results agreed well with the calculated values based on the reactor's operating history.

Introduction

Nickel-based alloys, with their superior properties of high-temperature strength, toughness, creep and corrosion resistance, are used as component materials in nuclear power reactors, and have been proposed for use in Gen-IV reactors, fusion reactors, and neutron spallation sources. Neutron radiation can damage the alloys by affecting the mechanical properties and microstructure. It is believed that direct displacement of atoms and gas generation from nuclide transmutations are the two principal mechanisms causing neutron irradiation damage to the materials [1]. While displacement damage occurs mostly with fast neutron collision cascades, transmutation through some nuclear reactions, such as 58Ni to 59Ni followed by 59Ni(n, α)56Fe by thermal neutrons, generates helium gas. The generated helium clusters to bubbles and voids which enhances grain boundary and precipitation boundary fracture as well as matrix cleavage and accelerates the embrittlement [2], [3]. Helium induced embrittlement is a great concern for commercial reactors where neutron dose in the core structural materials is high.

In CANDU® reactors, the hot pressure tubes (250°C-310°C) containing the fuel and the coolant are separated from the cool moderator (60°C-70°C) by a gas gap (CO_2). The calandria tube supports the pressure tubes through annulus spacers (garter springs) to ensure the separation of the two tubes. Spacers of some reactors were made of Inconel X-750, a nickel-based alloy. It was observed that spacers were becoming brittle with increasing operating times due to radiation damage caused by atomic displacement and helium and/or hydrogen generation[4],[5]. Therefore, thorough research into

the fundamentals of neutron radiation damage by helium and hydrogen generation in nickel-based alloys is needed for the assessment of reactor component lifetimes. For such research activities, development of analytical methods to accurately and precisely measure the helium and/or hydrogen content in irradiated nickel alloy materials becomes essential.

Earliest reported analytical methods for the analysis of radiogenic helium in irradiated materials involved a process of gas liberation by acid dissolution of the samples. These methods were usually carried out in a specially designed apparatus under controlled atmosphere of Ar or CO_2. The released gas was transferred to a sampling device where helium was separated out by condensing other gases in an activated charcoal trap under liquid nitrogen. Subsequently, helium was measured by gas chromatography (GC) or mass spectrometry (MS). This method has been applied to the determination of helium at 60 to 260 appm (atomic part per million) in irradiated beryllium oxide [6],[7]. Faster methods were developed later for determination of hydrogen and helium in irradiated materials [8]-[11]. In these methods, a small specimen was vaporized by heating under vacuum causing the release of helium. The released helium was determined by a quadrupole mass spectrometer system, and lower detection limits were achieved.

In general, vacuum fusion (VF) techniques have been developed for extraction of gaseous elements as gases from metals or alloys for their determination [12]. In VF, the samples are fused with a flux or bath metal in a crucible under vacuum, which results in the complete liberation of H, O and N as H_2, CO, and N_2 respectively with the addition of carbon to the flux. A variation of the VF technique is inert gas fusion (IGF) in which the fusion takes place under a stream of carrier gas instead of under vacuum for coupling with GC. IGF has been used successfully for studying the retained fission gas in irradiated oxide fuels [13],[14].

The transmuted helium in the Ni-based alloys is believed to remain in the bulk metal without much chemical bonding to the metal atoms, so it can be easily liberated by VF. Additionally, there are other advantages to extract He from radioactive specimens by vacuum fusion with a flux. Firstly, using the flux as a binary eutectic mixture, the extraction of the He by VF can be achieved at a lower temperature than the melting point of the metal/alloy specimen. Secondly, the small, highly radioactive specimen, is dispersed into of a large amount of inactive flux material and immobilized after the analysis. These advantages greatly help the radiation protection practises by providing effective radiation shielding and minimizing the vaporization and deposition of the radioactive materials inside vacuum chamber and by reducing the chances of radioactive contamination during waste disposal. MS is one of the primary analytical methods for analysis of small amounts of gaseous species. There are abundant choices of mass spectrometric inlet interfaces for a desired detection limit and an accuracy of the extracted and collected helium. In this work, a vacuum fusion technique is coupled with mass spectrometry to successfully determine the transmuted helium in neutron-irradiated nickel-based alloy samples.

Experimental

Reagents and Materials

Pure helium gas of 99.999% and 2%, 20% helium balanced by argon as calibration standards were purchased from Messer Canada. Tin capsules (□ 5 mm, H13 mm) were purchased from LECO Instruments ULC, Mississauga, ON - Canada. Platinum shot, 0.1-3 mm, 99.9% was purchased from either Alfa Aesar, Tewksbury, MA - USA or ESPI Metals, Ashland, OR - USA. Nickel and tin flux were purchased from Leco Instruments ULC, Mississauga, ON - Canada or Alpha Canada Inc., Etobicoke, ON - Canada. Zirconia grog used as heat insulation material was purchased from either Zircar Zirconia Inc., Florida, NY - USA or Zircoa, Solon, OH - USA. Graphite crucible, funnel, and quartz sample tube with conflat flange seal were all made in-house.

A radioactive nickel alloy material, coded as D2A in the Analytical Laboratories at CNL was used as quality control material (QCM). This QCM has a predicted helium concentration of 72 appm and was provided by the Material Sciences Branch at CNL. The QCM was used in testing the method during its development and used as a QC sample in subsequent sample analysis. The fuel channel spacer samples from CANDU reactors were provided from material surveillance projects and were prepared in the Hot Cell Facility and transported to the VF-MS laboratory.

Sample Preparation

The samples to be analyzed were obtained from irradiated Inconel X-750 alloy materials from CANDU® fuel channel spacers. The desired mass of the sample was selected by a compromise between the concentration of the He for a measurable amount of He and the ^{60}Co radioactivity for minimizing the radiation dose. The optimal sample mass, ranging from 0.003 to 0.05g, was selected to minimize the radiation dose rates coming from radionuclides, mainly ^{60}Co, while also producing measurable amount of He for an accurate determination. Usually, materials that have high He concentrations also have high ^{60}Co activity and vice versa. This characteristic of the samples facilitates using a large sample for low-helium concentration samples and a small sample for samples with high helium concentrations. The cutting, cleaning, and capsulating of the samples was performed in CNL's hot cell facility. The cut samples were cleaned with DI water, methanol, and acetone to remove potential surface contaminants. The cleaned samples were weighed on an analytical balance and if the mass was less than 20 mg, they were wrapped within pre-cleaned and weighed tin capsules. After wrapping, the total weight was taken to confirm the presence of the sample inside the tin capsule. The prepared specimens were transported from the hot cell facility to mass spectrometric analysis laboratory by a specially designed sample basket within a lead-shielded flask.

Instruments, Apparatus, and Measurement Method

The home-made high vacuum sample exchanger includes a 7-position carousel which can analyze up to 7 samples at a time. The VF apparatus, connected to the sample changer, was built in-house and

includes an induction heating system and infrared pyrometer purchased from Ambrell, Rochester, NY - USA. This part of the system was enclosed in a radioactive warm cell capable of shielding the radiation and containing any potential radioactive contamination during sample handling. The gas collection and handling system was also built in-house and described elsewhere [12, 15–16]. A diagram showing the various functional components of the system is given in Fig. 1. An inlet modified MS (Model Prima Pro, Thermal Scientific) was interfaced with the gas collection apparatus through a variable leak valve (Model ZLVM267R, VG Scienta).

The quantitation of helium in the collected gas was carried out with MS. The calibration of the MS was carried out by dosing a series of accurate amounts of pure, 20% He, or 2% He gas, depending on the concentration of the helium in the sample and the sample's mass. The volume of the dose chamber was calibrated against a calibrated glass bulb by gas expansion. The glass bulb's volume was calibrated by gravimetry with deionized water. Finally, the He concentration relative to the metal sample was calculated with the sample mass and reported in appm.

Notations in the figure, V_1 to V_7 are the high vacuum valves; P_1 to P_4 are capacitance monometers; CV_1 and CV_2 are calibrated volumes; T_1 and T_2 are turbo molecular pumps.

Results and discussions

Gas Release profile from vacuum fusion

In analysis mode, the VF-MS system described above follows a sequence of steps starting with preparation of the crucible, loading sample specimens into the sample exchanger, and ending with released helium being analyzed by the mass spectrometer. The system can also be run in a monitoring mode with valves V_5 and V_6 (Fig. 1) open and the MS monitoring continuously. Consequently, the MS records the accumulated gas released from the VF process with time elapsed after the specimen is dropped into the crucible. Figures 2 displays a profile obtained from dropping a 0.0016 g specimen taken from an active CANDU® fuel channel spacer which had approximately 30,000 appm (3 atom%) helium. In this case, the flux used was 10 g of Pt (85%) - Sn (15%) mixture and the fusion temperature was 1,450°C. The sample was dropped approximately 0.4 minutes after the mass spectrometer started collecting the signal of the helium gas.

Figure 2 shows that the helium signal increased steeply in the first 2 minutes and reached a plateau. It indicates that the helium was released immediately after the sample was dropped into the crucible. After about 2 minutes, the monitored helium signal started to decrease with time. The overall signal profile of the gases, which are monitored, is a function of the combination of gas release, gas consumption by the MS measurement, background emission from the fusion, and the leakage from atmosphere into the vacuum chamber. For helium, the background emission and the air leakage are considered negligible compared to its release and consumption by the MS measurement. A continuous but very gradual decrease in intensity after a plateau with the time elapsed indicates that the He was completely released

within the first 2 minutes, and a small amount of it was consumed by the mass spectrometric measurement.

Optimization of Key VF-MS Parameters

Based on a long history of successful determinations of H, O, and N in many different metals and alloys including U, U-Si, U-Mo, U-Al, U-Si-Al alloys, zircalloy, and steel samples by VF-MS using 85% Pt - 15% Sn as flux at CNL Laboratories [13], this mixed flux was chosen for the determination of helium in nickel-based alloys. Because the sample specimens were a nickel-based alloy, a 85% Ni – 15% Sn flux mixture was also used and tested. The two main parameters in VF, the fusion temperature and the time for gas evolution and collection were tested using the D2A in-house QC materials. Temperature ranges from 1,350°C to 1,800°C were tested for the Pt - Sn flux. The lowest temperature (1,350°C) was the minimum required as it coincided with the eutectic temperature of the 80% Pt – 20% Sn mixture. The upper limit of 1,800°C was the limit for safe operation of the apparatus. With Ni-Sn flux only 1,450°C was tested as the fusion temperature.

Table 1 lists the measured helium concentrations from D2A specimens under different vacuum fusion conditions. The average measured value by VF-MS using Pt-Sn flux was 70 appm (one standard deviation of 3 appm; n = 6), which is not statistically different from the predicted value of 72 appm ($t = 1.16$, less than $t_{0.05, 4}=2.78$). The same conclusion holds if comparing the average value measured by this method with the measured value of 69 appm from another laboratory ($t = 1.26$, $t_{0.05, 4}=2.78$). The only test using nickel-tin flux resulted in a helium concentration of 71 ± 2 appm (1SD). The good agreement of the in-house QC material D2A with the determined helium concentration values by this VF-MS method, the predicted value, and the result from another laboratory suggests that the release of He from the samples was complete under all sets of fusion temperatures, collection times, and using both types of fluxes.

Based on the test results obtained in this work, either Pt - Sn or Ni - Sn flux can be used. Ni - Sn flux was used in subsequent analyses owing to its low cost. Fusion temperature of 1,450°C and release time of 6 minutes were determined as optimal to perform complete He extraction and analysis by VF-MS.

Table 1
Measured Helium Concentrations Under Different Fusion Temperatures and Times for D2A Specimens.

Specimen Mass, g	Flux	Fusion Temperature, °C	Fusion time, min	He, appm		
				Measured by this method	Predicted	Measured by Another Laboratory [10, 11]
0.0515	Pt-Sn	1,350	5	73 ± 5	72*	69*
0.0589		1,500	6	73 ± 2		
0.0626		1,600	6	68 ± 2		
0.0419		1,800	5	67 ± 3		
0.0487		1,800	5	70 ± 3		
0.0499	Ni-Sn	1,450	5	71 ± 2		

* Uncertainty not available

Analysis of Reference Material and Long-term Performance

Although D2A was not a certified reference material (CRM), nor a standard reference material (SRM), it was adequate for evaluating the performance of the method based on its uniformed helium concentration produced through neutron activation. Its predicted helium content was 72 appm without an uncertainty given. There have been 42 valid He measurements performed over a period of more than 6 years - from March 2018 to July 2024. A weighted mean and its uncertainty were calculated as 72.65 ± 0.54 appm using square of the reverse standard deviation as the weight. A comparison of the weighted mean with the predicted value was performed. The t-statistic was found to be 1.2 which is less than the critical value of 2.0 at the 95% confidence level and suggests that there is no significant difference between the measured mean and the predicted value. Figure 3 illustrates the individual measured values with uncertainty (2s), the weighted mean value, and the predicted value. The relatively higher uncertainty observed for all the measurements performed in 2024 compared to the measurements performed from 2018 to 2023 was mainly caused by the differences in weights of the specimens. The specimen weight used before 2023 was 55 ± 23 mg, while for 2024 it was 5.5 ± 1.7mg.

Detection Limit and Accuracy

The analysis method developed at CNL was targeted to measure the concentration of transmuted helium in the irradiated CANDU reactor fuel channel spacer materials in which the helium concentration is tens of thousands appm. Achieving a lower detection limit was not pursued, although smaller

measurement uncertainty was desired. As mentioned above, irradiated material containing high levels of helium usually also contains high radioactivity which generates high radiation dose rates. This VF-MS technique permits the use of a small specimen to get sufficient helium for an accurate and precise measurement and the low enough radioactivity for safe sample handling. As the specimen mass becomes small, the uncertainty from weighing the specimen becomes a major contributor to the overall analysis uncertainty.

Focusing on quantitation of the amount of helium by MS, a limit of detection (LOD) is defined as 3 times the standard deviation of the blank signal, as recommended by IUPAC. The LOD for He by MS was estimated to be about 2×10^{-9} moles of He. The method detection limit (MDL) is the smallest helium concentration (appm) that can be measured in a specimen of certain mass. Table 2 lists the MDL by different specimen masses. Currently, the smallest manageable specimen mass handled in a hot cell environment is around 0.002 g. Consequently, the maximum MDL for analysis of materials of high-level helium and radioactivity is about 56 appm of helium. MDL becomes lowers for less radioactive samples for which a large specimen mass is used. The analyses of the D2A QCM specimens presented in Table 1 used 0.05g samples, having MDL's as low as 2 appm.

Table 2
MDL of Determination of He by VF-MS Using Different Specimen Masses

Specimen Mass, g	**0.0015**	**0.01**	**0.05**	**0.1**
MDL, appm	56	11	2	1

The uncertainty from the MS's quantitation of helium and uncertainty from weighing the specimen were found to be the two major contributors to the overall VF-MS measurement uncertainty. Table 3 shows the breakdown of these two uncertainty components for a few of the samples considered in this work. The uncertainty contribution from weighing was much larger for the 4 samples with masses from 0.0017 to 0.0036 g than that of the D2A QCM that used much higher masses. The uncertainty from the MS was consistently below 1% for the helium quantity measured at 9.64×10^{-8} moles but increased to 2% from the analysis of the D2A specimen of lower mass which released 3.72×10^{-8} moles of helium. Overall, the major uncertainty contributor to the analysis of small samples (i.e., mg masses) comes from the weighing of the samples.

Table 3
Breakdown of Uncertainty Components for VF-MS Determination of Helium in Some Neutron-Irradiated X-750 Alloy Specimens

Specimen	Mass, g	Rel. Unc. Weighing	He, moles	Rel. Unc. MS Anal.	He, appm	Rel. Unc. Overall
D2A	0.0750	0.1%	$(9.64 \pm 0.11) \times 10^{-8}$	0.7%	73 ± 1	1.1%
D2A	0.0293	0.3%	$(3.72 \pm 0.08) \times 10^{-8}$	2.0%	72 ± 2	2.2%
AECL 201-3	0.0025	4.0%	$(4.81 \pm 0.05) \times 10^{-7}$	0.6%	10,900 ± 500	4.2%
AECL 201-3	0.0017	5.8%	$(3.22 \pm 0.04) \times 10^{-7}$	0.7%	10,600 ± 600	6.1%
AECL 25 – 3	0.0019	5.3%	$(1.06 \pm 0.11) \times 10^{-6}$	0.7%	31,600 ± 2,000	5.5%
AECL 25 – 3	0.0036	2.8%	$(1.93 \pm 0.23) \times 10^{-6}$	0.8%	30,600 ± 1,000	3.1%

Applications

As mentioned in the introduction section, measurement of transmuted helium in neutron irradiated nickel alloys was necessary to investigate the radiation effects of the materials for reactor component's life management. The developed method was applied to analyze 128 CANDU® fuel channel spacer specimens so far. Among them 107 specimens were from the removed CANDU® ex-service Inconel X-750 annulus spacers and 21 were from HFIR (High Flux Isotope Reactor) capsule. A comparison between the measured He concentration and the calculated He concentration of these samples is shown in Fig. 4. The horizontal axis represents the calculated (and predicted) He concentration based on the relationship between He generation and total dpa (displacement per atom), a measure of neutron dose. The vertical axis represents the measured He concentration. Figure 4 shows good agreement between the calculated (predicted) He content and measured He content for all 128 samples. Some of the HFIR capsule specimens were measured using a large specimen mass due to their lower radioactivity and had the best agreement between their measured and the calculated values. The uncertainty for the predicted He concentration was due to the neutron spectrum and the neutron flux, both estimated from reactor operation history. The prediction of He concentration is beyond the scope of the development of this analytical method and is not discussed in this work.

Conclusions

A vacuum fusion-mass spectrometric method (VF-MS) was developed for the determination of the transmuted helium in neutron irradiated reactor materials. Either Pt(85%) - Sn(15%) or Ni(85%) - Sn(15%) can be used as the flux material. The optimal parameters for performing He extractions and measurements were at 1,450°C and 6 minutes of fusion time. The method was validated by comparing results obtained from analyzing a quality control material using this method, an independent laboratory using a different method, and by the calculated values from reactor operating history. For highly radioactive materials, a specimen as small as 0.003 g can yield a measurement with reasonably low uncertainty. Use of a larger sample, if allowed by administrative radiation field limits, can provides lower detection limits and lower analysis uncertainties. The developed method has been applied to determination of He in current commercial surveillance programs on removed CANDU® ex-service Inconel X-750 annulus spacers. The measured results agreed well with the predicted results based on the relationship between He generation and total dpa (displacement per atom), a measure of displacement damage.

Declarations

Author Contribution

Y.S. The Scientist who conducted the research who wrote the manuscript.R.M. The technologist who performed the experiments.

Acknowledgement

The authors would like to thank Dr. Grant A. Bickel, Material Science Branch of CNL, for providing the calculated helium concentration values for the CANDU© fuel channel spacer specimens and HFIR capsule specimens analyzed, enabling the validation of the developed method.

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Figures

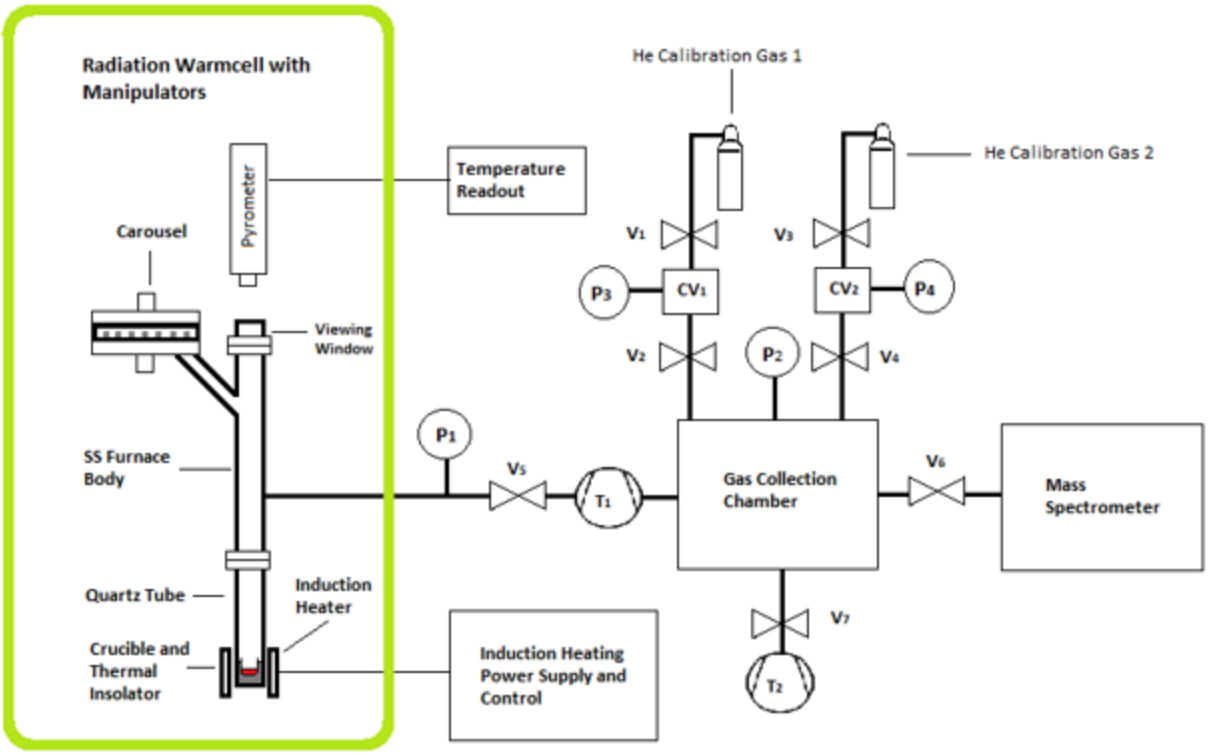


Figure 1

Block diagram of the VF-MS system at CNL.

Notations in the figure, V_1 to V_7 are the high vacuum valves; P_1 to P_4 are capacitance monometers; CV_1 and CV_2 are calibrated volumes; T_1 and T_2 are turbo molecular pumps.

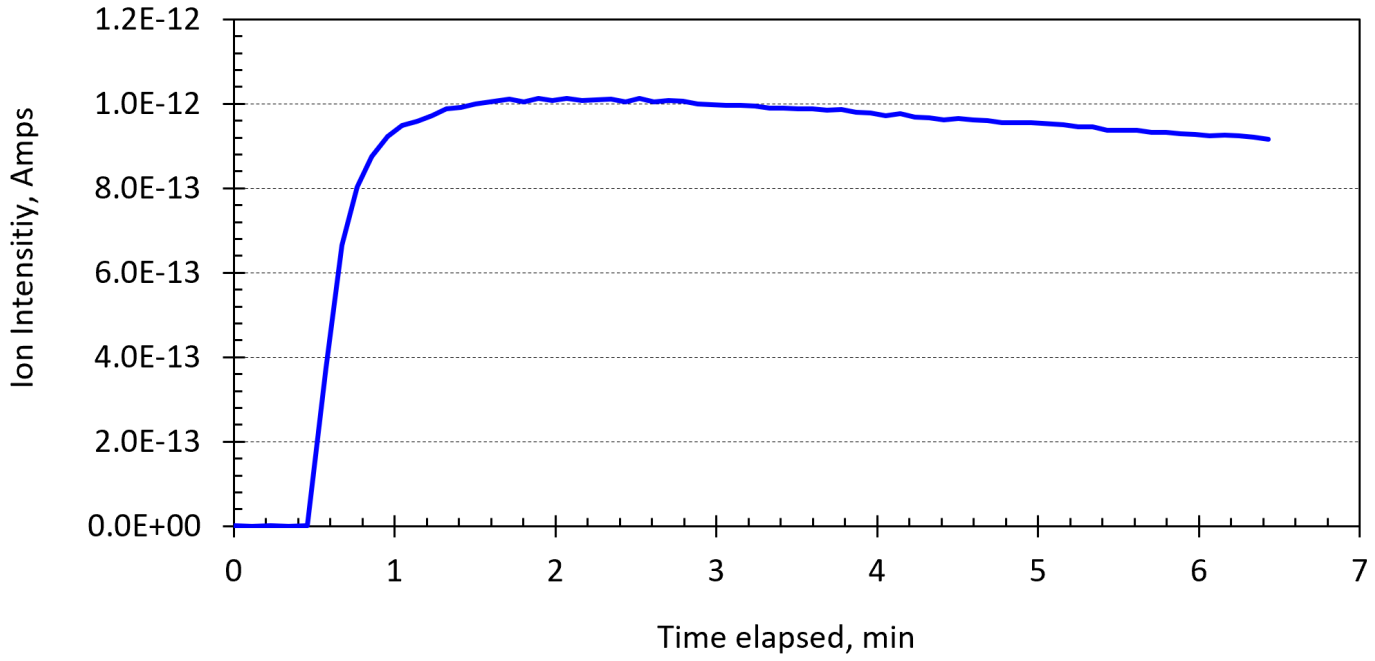


Figure 2

Helium release profile from Inconel X-750 alloy specimen vacuum fused with Pt-Sn flux under 1,450 °C

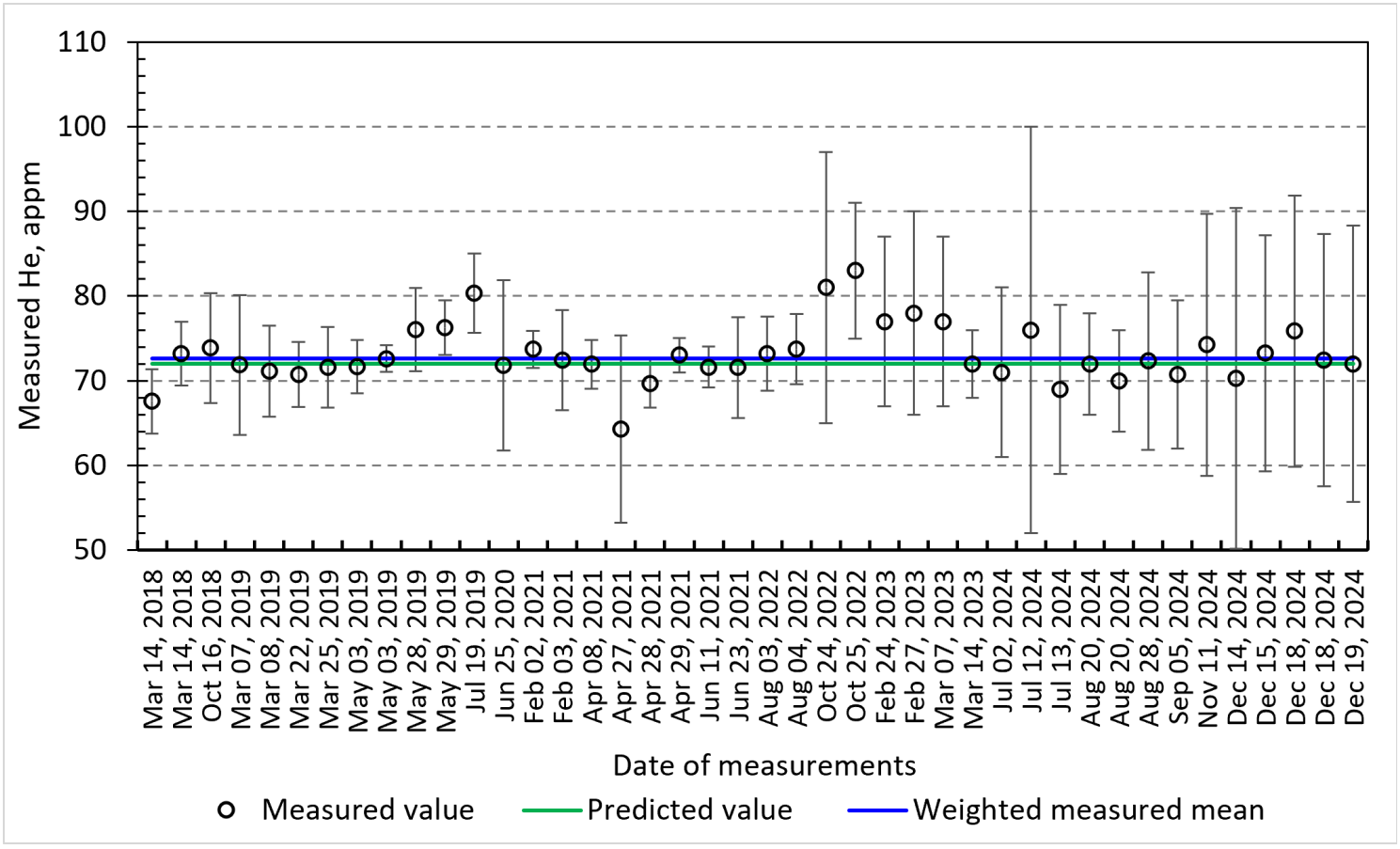


Figure 3

Individual measured, weighted mean, and predicted helium concentrations for reference material D2A over a period of 6 years (2018-2024)

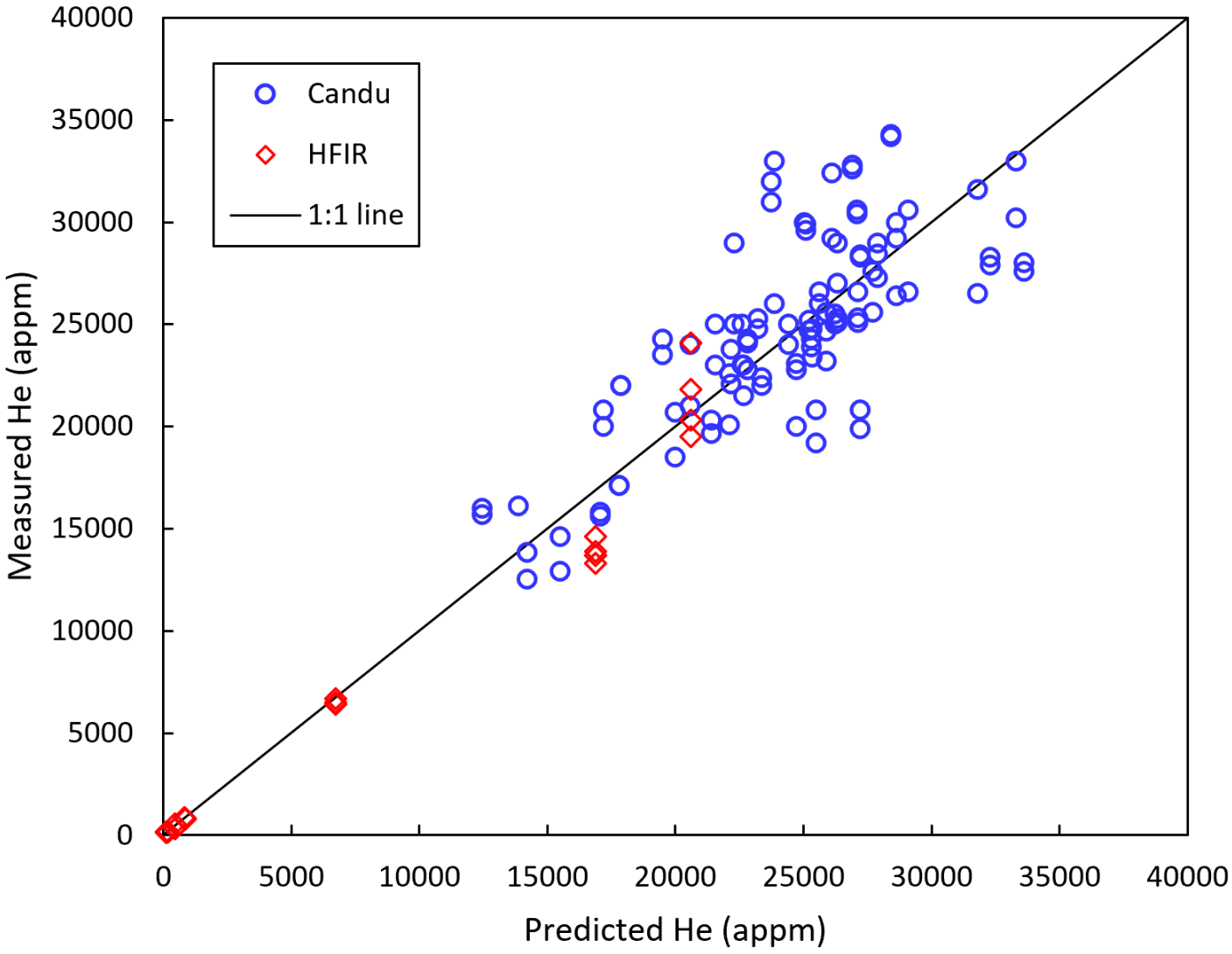


Figure 4

Predicted vs. Measured He content in 128 samples analyzed