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Application of an Online Chromium Reduction System for D/H Analysis of Water Samples with Large Isotopic Variations Using Conventional Mass Spectrometer

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Abstract

We present an online chromium (Cr) reduction system for measuring the D/H ratio of water samples exhibiting significant isotopic contrast, where the memory effect cannot be overlooked. Memory compensation is incorporated into the analysis procedure to mitigate this effect, allowing the utilization of injection results that would otherwise be discarded due to the memory effect. This approach enables a faster analysis and an increased sample throughput. Additionally, crucial aspects of the chromium reduction system aimed at maximizing the number of samples that can be analyzed per recharge of the chromium reactor, have been brought out. To achieve this, the furnace is configured for a uniform temperature profile, Cr powder is mixed with quartz glass granules, and the furnace is kept at continuous operation. This configuration has allowed us to achieve reproducibility better than ±0.15 ppm for two injections by incorporating memory compensation and drift correction in the analysis procedure. Moreover, the present computer-controlled sample inlet system is designed for a continuous operation (24/7) allowing us for a rapid sample analysis, with analysis time per injection being approximately 6 to 7 minutes.

Keywords: Deuterium/hydrogen (D/H) analysis, mass spectrometry, chromium reduction, sample inlet system, isotopic contrast

INTRODUCTION

The mass spectrometer in our laboratory is equipped with an on-line uranium (depleted uranium) reduction system for deuterium/hydrogen (D/H) analysis of water samples. It is utilized to analyze a large number of water samples with large isotopic contrast on a regular basis. While the uranium reduction system offers the advantage of analyzing large number of samples per gram of uranium metal, challenges arise from handling radioactive materials and encountering high memory effects, etc. In response to these challenges, we have decided to explore alternative sample reduction/handling options. The chromium reduction method has advantages such as, low memory effect, excellent precision of measurement, and suitability for automation, which is why it has been selected for our application.

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The feasibility of the development of Cr reduction for D/H analysis of water sample was first demonstrated in 1996 by Gehre et al. [1], although the method had been known for a long time.

Subsequent improvements were reported by Donnelly et al. [2] and Nelson and Dettman [3]. Further advancements were made by Morrison et al. [4] and Itai et al. [5], who developed a Cr reduction system in which Cr metal powder is mixed with silica quartz granules to facilitate the smooth flow of hydrogen through the reactor. We have adopted this concept, as it allows for the maximum number of samples to be analyzed per chromium recharge. This paper provides a detailed description of the Cr reduction system we have developed.

All previously reported Cr reduction systems are designed for samples with relatively similar isotopic composition (variations: 1–2 ppm), where the memory effect can safely be ignored. However, when analyzing samples with large isotopic variations (~30 ppm), the memory of the previous sample must be either removed through repeated injection or compensated during the analysis procedure. Repeated injection slows down the analysis and increases Cr consumption, making memory correction the preferred method. This paper discusses the implementation of memory compensation and finally, analysis results for two injections of unknown samples are presented. The system's performance is evaluated in terms of memory effect, precision of measurement and analysis time.

In summary, this paper presents the development and validation of an on-line Cr reduction system integrated with a conventional mass spectrometer, focusing on improvements in sample throughput, precision, and memory effect correction. This work aims to deliver a reliable system for high-precision D/H analysis under a range of isotopic conditions.

EXPERIMENTAL

Chromium Reaction Tube and High-Temperature Furnace Configuration

The construction of the chromium (Cr) reduction system is a carefully orchestrated arrangement of components aimed at ensuring optimal efficiency and controlled reduction of water samples. The system operates based on the fundamental reduction reaction as:

$$2\mathrm{Cr}\,(s) + 3\mathrm{H_2O}\,(l) \rightarrow \mathrm{Cr_2O_3}\,(s) + 3\mathrm{H_2}\,(g) \qquad (1)$$

The configuration of the reactor is like the one implemented by Itai et al. [5]. It consists of an 85 mm long, 12 mm outer diameter (OD) quartz tube with both ends terminating in 6 mm OD tubes. The top end of the reactor is sealed with a Cajon Ultra Torr union (¼″ to ¼″), wherein the 'O' ring in the upper half of this union is replaced by low bleed septum for sample injection purposes. The lower end of the rector connects to a ¼″ Cajon Ultra Torr coupling of the sample inlet system. To prevent the escape of fine reaction particles into the high vacuum side, the lower portion of the reactor is sealed with quartz wool. This also serves to securely hold the chromium powder in place. The schematic diagram of the furnace is shown in Figure 1.

The reaction tube is placed in a furnace that operates at 900 °C to ensure the complete reduction of the water sample. The furnace design, optimized for an operating temperature of 900 °C, adopts a vertical placement with carefully engineered glass and metal connections. The furnace is constructed from a quartz tube (20 mm OD, 125 mm length) wrapped with Nichrome heater wire, optimized for uniform temperature distribution. The wire is tightly wound with a smaller pitch near both ends and with a larger pitch at the center, enabling homogeneous temperature distribution across the length. Aluminum plates, positioned at both the ends of the furnace, serve to support the reaction tube, and restrict heat flow from the furnace. The temperature distribution of the furnace (at 800 °C), measured using a K type thermocouple, is depicted in Figure 2.

This furnace design ensures the complete reduction of water samples within a well-insulated and temperature-regulated environment in the entire volume of the reaction tube with an effective volume of 10 $\mathrm{cm^3}$.

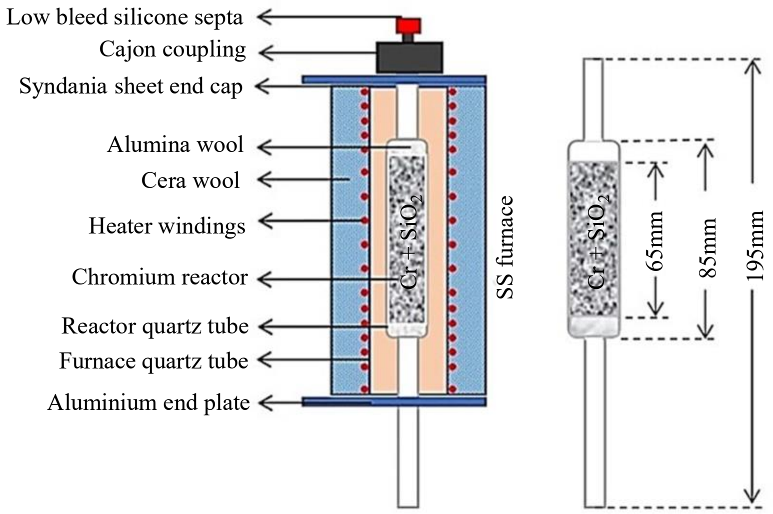

Figure 1. Diagram of chromium reaction tube and high-temperature furnace.

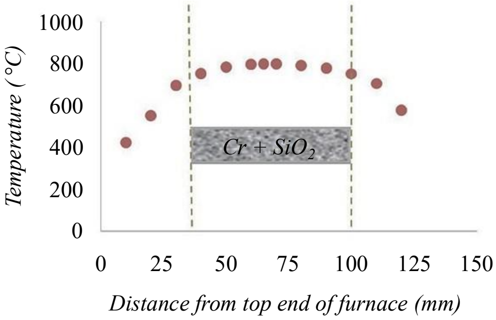

Figure 2. Temperature distribution of the furnace along its length.

The Cr reactor is filled with a homogeneous mixture of Cr powder (60 mesh size) and quartz glass granules (1–2 mm diameter) in the proportion of 8:1. The inclusion of quartz (SiO_2) granules within the mixture facilitates the unobstructed flow of hydrogen gas. Without this addition, gas flow can become restricted over time, as the formation of Cr_2O_3 may lead to cementation and subsequent blockage. This obstruction negatively impacts the system performance, particularly after several injections. To ensure maximum conversion efficiency of the Cr reactor, the furnace is continuously maintained at 900°C. Additionally, the presence of quartz granules in the reactor simplifies the removal of chromium oxide, allowing the reactor to be easily cleaned and reused.

Isotope Ratio Mass Spectrometry and Sample Inlet System and Analysis Procedure

The mass spectrometer (MS) in our lab is small footprint instrument developed for Hydrogen isotope (D/H) analysis of water and hydrogen gas sample [6]. It features an electron impact ion source, a magnetic sector analyzer, Faraday cup collectors, and electronics subsystem for MS operation and control. Vacuum of this instrument is maintained by a triode sputter ion pump (140 LPS). As this is a dedicated instrument for hydrogen isotope analysis, its high sensitivity is achieved at the cost of lower resolution, allowing us to obtain an M2 (m/e = 2) ion beam intensity of 3.5E-9 A, even for a sample size as small as 0.5 µL.

The computer-controlled chromium reduction-based sample inlet system (SIS) is coupled to the MS (as shown in Figure 3). The SIS consists of a high-temperature chromium reactor, a variable volume reservoir (VVR for H_2 gas holding and sample pressure adjustment), a pressure sensor, and vacuum pumps (for fore vacuum and high vacuum). The reactor is operated continuously at 900°C for maximum chromium efficiency [7].

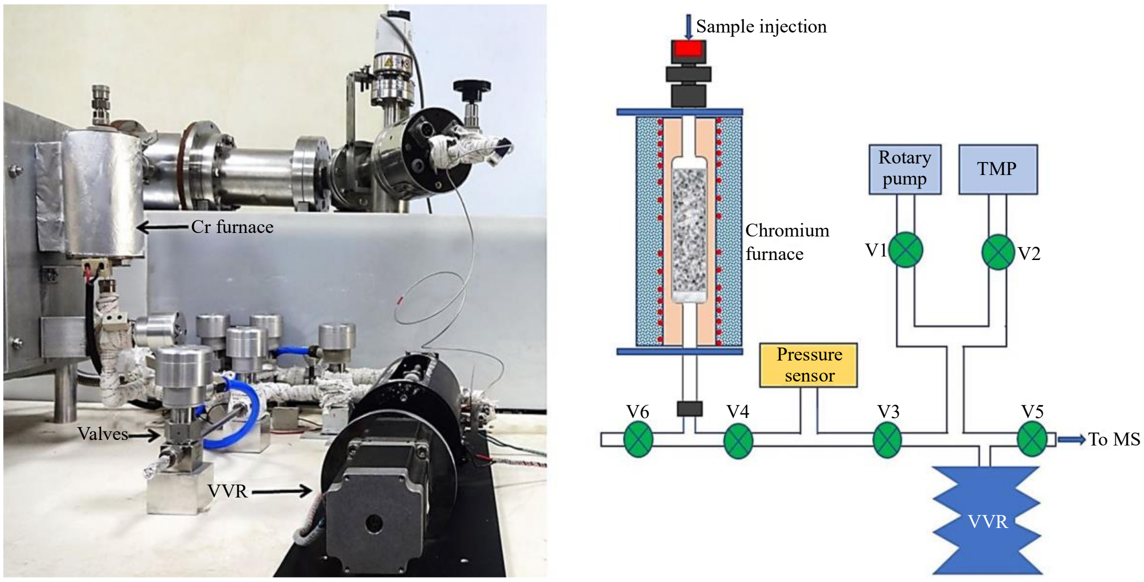

Figure 3. Sample inlet system (SIS) photograph and SIS schematic diagram.

24/7 Operation: Even when the MS and SIS are turned off, the chromium furnace remains on. A dedicated fore-vacuum pump and temperature control system are provided to support continuous furnace operation during these periods.

During the sample analysis, various sources of error (such as fractionation, drift, etc.) contribute to the overall uncertainty in the measurement of the isotope ratio [5]. To minimize these errors, a reproducible analysis procedure is followed, including fixed timings for water reduction, signal stabilization, and gas expansion in the VVR. Each injection analysis takes approximately 6 to 7 minutes.

MEMORY COMPENSATION

During a series of multiple injections of a given sample, the measured isotopic ratio progressively increases, for example, from 0.98 to 0.99, and then to 0.995 of the final value. This enhancement occurs due to the residual influence of the previously analyzed sample, a phenomenon known as the “memory effect” [8]. To use injection data affected by memory, the data need to be corrected for this effect. With memory compensation, injection results that would otherwise be discarded are utilized, and it results in faster analysis and increased sample throughput. The memory-corrected ratio can be derived by solving a linear mixing equation for each injection:

$$R_{\text{meas}} = F_m \times R_n + (1 - F_m) \times R_{n-1} \tag{2}$$

where R_{meas} is the experimentally measured ratio for the mth injection of the nth sample, R_{n-1} is the isotopic ratio from the previous sample, F_m is the memory coefficient for the mth injection, and R_n the value to be calculated, is the memory-corrected ratio for the nth sample.

To determine the memory coefficients for the first and second injections, two samples with high isotopic contrast are repeatedly analyzed. The memory coefficients for each injection are then calculated using Equation (2). The average values from multiple runs are used for correcting unknown sample measurements. Typical values are:

- *Average first memory coefficient:* 0.9731 (97.31%)
- *Average second memory coefficient:* 0.9913 (99.13%)

These memory coefficients are subsequently applied during the sample analysis for the memory compensation. As chromium gets consumed, there is slight change in memory effect also. Hence memory coefficient needs to be evaluated periodically. If measured precision for two injection analyses is less than ±0.15 ppm, then memory coefficients need to be re-evaluated.

Table 1. Analysis results of two samples after the drift and memory corrections.

S.N.	Injection no.	Ratio (ppm)	Ratio (corrected for memory) (ppm)	Ratio (corrected ratio for drift) (ppm)
Reference	1	129.36		129.41
	2	129.59		129.54
	Mean	*129.48*		*129.48 ± 0.07*
Sample 1	1	144.79	145.22	145.12
	2	145.38	145.52	145.37
	Mean		*145.37*	*145.25 ± 0.13*
Sample 2	1	156.49	156.8	156.6
	2	156.6	156.7	156.46
	Mean		*156.75*	*156.53 ± 0.07*
Reference	1	130.35	129.62	129.33
	2	129.96	129.72	129.38
	Mean		*129.67*	*129.36 ± 0.05*

Our instrument has a single inlet system, and isotope ratio are expressed in ppm (parts per million). Drift that occurs in analysis result needs to be corrected to achieve reproducible results. In dual inlet systems, drift correction is not required as it is taken care by measuring difference between the sample and the reference. In our instrument, a known reference sample is analyzed periodically after every few unknown samples. Drift in the reference sample study is then utilized to correct other sample results, as shown in Table 1. Both memory correction and drift correction are crucial to get reproducible analysis result [9, 10].

ANALYSIS RESULTS

Unknown samples and a known reference are analyzed together to remove instrumental drift and to obtain accurate results. Generally, 2 to 5 samples are analyzed between each set of reference analysis. Table 1 (given below) shows the analysis of two unknown samples. First, the reference sample was analyzed, followed by two unknown samples, and finally, the same reference sample was analyzed again. Each sample was injected twice, and the isotope ratios were recorded, as shown in Table 1. Memory correction was then applied using Equation 2 and utilizing the previously determined memory coefficients. The memory-corrected ratios are presented in the fourth column in Table 1. Next, a drift correction was applied, using data from multiple analyses of a reference sample. The results, corrected for both memory effects and instrumental drift, are shown in the last column in Table 1.

- From the analysis of the two samples, the following observations were made:
- The precision of measurement is better than ±0.15ppm for two injections.
- The memory effect is 2.69% for the first injection and 0.87% for the second injection.
- Above results are for two injections per sample analysis. If a higher precision is required, then sample can be analyzed with three to four injections per sample.

CONCLUSION AND FUTURE DEVELOPMENTS

This study presents a Cr reduction system that addresses the primary limitations of uranium reduction system for D/H analysis of water samples. The new system provides high precision of measurement and reduced memory effects. Memory effect is 2.69% for the first injection and 0.87% for the second injection. Memory and drift corrections enable accurate results even for samples with extensive isotopic variation. With the new reduction system, a greater number of samples are analyzed in a given time with better precision of measurement. The precision of measurement is ±0.15 ppm for two injections. For higher precision, three to four injections per sample can be utilized. The performance of this system is comparable with similar system used elsewhere. Commercial instrument used for such application has precision of ±1‰, which corresponds to ±0.15 ppm [3].

In the present system, sample size reproducibility is poor due to manual sample injection and it affects the precision of measurement to some extent. It is planned to use sample injector along with an auto sampler for improved performance and unattended analysis of large number of samples.

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