Some practical aspects of an on-line chromium reduction method for D/H analysis of natural waters using a conventional IRMS

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Some practical aspects were investigated for an on-line chromium reduction technique for measurement of D/H variations of natural waters using a conventional isotope ratio mass spectrometer. They include the configuration of the reaction system, the precautions taken before mass spectrometric measurement, the reproducibility of δD measurement, memory effects and salt effects. Approximately 150 water samples of 2 μ l can be run with Cr powder (60 mesh) weighing approximately 16 g mixed with quartz glass sand (10 mesh). The mixture functions to avoid choking of the Cr reactor due to volume increase as Cr oxidation proceeds. The Cr powder-quartz glass sand mixture is placed in the middle of a quartz glass reaction tube and heated to $>800^{\circ}\text{C}$. The reproducibility is *ca.* $\pm 0.5\%$ if care is taken for the above precautions and memory effects. This system can be easily installed on a conventional IRMS at low cost.

Keywords: on-line, chromium reduction, D/H analysis, natural water, IRMS

INTRODUCTION

Hydrogen isotopic variations have been widely used for tracing water in hydrosphere and biosphere in recent years. Hydrogen isotopic ratios (D/H) are commonly measured with either conventional IRMS (isotope ratio mass spectrometry) or continuous flow IRMS using hydrogen as an analytical gas. Several methods have been proposed to prepare hydrogen from water. These are reduction by uranium (Bigeleisen *et al.*, 1952), zinc (Coleman *et al.*, 1982; Kendall and Coplen, 1985), manganese (Tanweer and Han, 1996) and chromium (Gehre *et al.*, 1996; Donnelly *et al.*, 2001; Nelson and Dettman, 2001; Morrison *et al.*, 2001), and by a H_2 - H_2O equilibration technique (Ohsumi and Fujino, 1986; Horita, 1988; Ohba and Hirabayashi, 1996). Each method has its own advantage and disadvantage. The uranium reduction method can produce stable data but requires time-consuming off-line operation on a vacuum line using a mercury Toepler pump. Use of mercury is not welcomed from the environmental point of view. Recently an automated on-line system using uranium has been reported (Vaughn *et al.*, 1998). Metallic uranium is getting more difficult to obtain due to regulations on nuclear materials. The zinc method has no memory effect because the reduction of water is done in a sealed tube. However, care

has to be taken with the choice of zinc that reacts easily with water and with the zinc/water ratio that affects D/H ratio of the resulting H_2 (Florkowski, 1985; Hayes and Johnson, 1988; Tanweer, 1990; Noto and Kusakabe, 1995). The H_2 - H_2O equilibration technique has a big advantage because the D/H and $^{18}\text{O}/^{16}\text{O}$ ratios of the water sample can be efficiently measured on a same sample using a common, on-line equilibration apparatus. There is, however, a constraint that temperature of the H_2 - H_2O equilibration must be strictly controlled because there is an extremely large D/H fractionation factor between H_2 and H_2O with a large temperature dependence. The chromium method is used with both on-line and off-line systems (Gehre *et al.*, 1996; Donnelly *et al.*, 2001; Nelson and Dettman, 2001). A fully automated on-line system is now available on a commercial basis (Finnigan MAT, 1997; Morrison *et al.* (2001) of VG Instruments). These commercial systems are basically designed for measurement of a large number of samples of more or less similar isotopic compositions. Note that these commercial systems are very expensive. In this note, we report some practical aspects of a simple, manually operated, on-line Cr reduction system that can be attached to a conventional mass spectrometer at low cost. We present the configuration of the reaction tube, the reproducibility, effective methods for rapid reaction, the memory effect and salt effects for the system that is attached to a VG SIRA10 mass spectrometer at the Institute for Study of the Earth's Interior, Okayama University. This system is used to determine the D/H variations of natural waters.

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MATERIALS AND METHODS

Reaction tube and chromium furnace

The overall configuration of the reaction tube and furnace is similar to that described by Donnelly *et al.* (2001). Our system, however, includes some improvements described here. The Cr reduction system used is illustrated in Fig. 1(a). A mixture of approximately 16 g of Cr metal powder (60 mesh, 99.99% pure, Mitsuwa Chemicals, Co. Ltd., Japan) mixed well with ~2 g of quartz glass sand (~10 mesh) was placed in the middle of a reaction tube made of quartz glass (Fig. 1(b)). The quartz glass sand was intended to facilitate smooth gas flow inside the tube for rapid and complete reduction, otherwise gas flow became less smooth with time due to choking of the flow path through formation of chromium oxide that has a specific volume almost twice as large as that of metallic chromium (at room temperature). Our preliminary test indicated that performance of the Cr reactor without quartz glass sand became deteriorated after only 28 runs with insufficient recovery of hydrogen gas and poor reproducibility in δD . The chromium-quartz glass mixture was sandwiched by quartz glass wool. Contamination of the mass spectrometer inlet system by fragmented quartz glass wool and Cr powder was avoided by fritted glass placed at one end of the tube (see Fig. 1(b) for size details). The glass tube has an end with an outside diameter of a 1/4 inch. The other end has a 1/2 inch outside diameter in order to make the use of a Swagelok connection. A vacuum of $1E-3$ mbar was attained by pumping the tube with the rotary pump in the mass spectrometer inlet system. Sample water was introduced into the reaction tube by a micro syringe through a silicon rubber septum. The septum was held in a stainless steel holder by the Swagelok connection. No leakage of air into the reaction tube through the septum when sample was introduced with a syringe, but the septum should be replaced with a new one to avoid a possibility of air leakage when Cr is renewed. The other end of the reaction tube was connected to the mass spectrometer inlet system through a valve FV as shown in Fig. 1(a). The hydrogen gas sample prepared off-line can also be attached to the mass spectrometer inlet system through a valve SS when required.

The furnace was placed horizontally over the reaction tube (Fig. 1(a)). This position secured a more homogeneous temperature distribution along the reaction tube than the vertical position adopted by Donnelly *et al.* (2001). We used a quartz glass tube of 20 mm O.D. as a core over which 300 W Nichrome wire was wound. The wire density was less in the middle part relative to both ends in order to attain homogeneous temperature distribution. Temperature was measured with an alumel-chromel thermocouple attached to a temperature controller. Aluminum plate was attached at both ends of the furnace to reflect thermal radiation from a red-hot Cr furnace. Tempera-

Fig. 1. (a) Configuration of the on-line chromium reduction system, (b) shape and size of the quartz glass reaction tube, and (c) temperature distribution of the furnace.

ture distribution within the furnace of our system when set to 800°C is shown in Fig. 1(c).

All of the required components for the present system are inexpensive. The total costs are less than 1/100 of those for a commercially available equivalent, although our system is manually operated.

Optimum conditions for reduction

Sample size Since a large amount of water consumes more chromium and takes longer to react, the minimum amount of water was examined first. After many trials using our system, we found that the optimum sample size of approximately 2 μ l of water was obtained with a stable $M/e = 2$ ion beam intensity of $5E-9$ ampere. The sample size can be reduced down to 1.5 μ l.

Reaction period and temperature Reduction starts immediately after water was introduced into the reaction tube through the rubber septum if temperature of the Cr fur-

Fig. 2. Change in δD_m values with equilibration period before admitting H_2 gas into the sample inlet variable volume.

nance was high enough. Hydrogen gas pressure rose with time and reaches a steady level after some time, usually around 10 min. The H_2 gas pressure was monitored by a pressure transducer that was placed between valves FV and SI (SS is always closed, Fig. 1(a)). We found that the minimum reaction period was 12 min when the transducer reading became perfectly stable. However, a longer reaction period, e.g., 15~20 min, may be required as oxidation of Cr proceeds.

Equilibration period An apparent isotopic fractionation is associated when H_2 gas in the volume between the reaction tube-valve SS-valve SI is expanded into a variable volume within the mass spectrometer inlet system (Fig. 1(a)). This fractionation may be caused by isotopic gradient within the volume where a higher proportion of isotopically “light” hydrogen produced from early stage evaporation of water exists in the forefront relative to the other end. Isotopic equilibration between the produced hydrogen and the remaining water vapor might also contribute formation of isotopically light hydrogen in the initial stage of the reaction. This suggests isotopic homogenization is required before mass spectrometric measurement. Since it takes long time to attain complete mixing in a large volume, it is important to expand the gas initially to a minimum volume, i.e., valve SI is kept closed and then valve FV is opened. At this stage, we waited for some time for isotopic homogenization. We examined this homogenization period before starting mass spectrometric measurement. After an appropriate period, valve SI was opened to expand the gas into the minimized sample variable volume. Following an additional 1 min, the variable volume was adjusted to obtain an optimum beam intensity. Figure 2 illustrates the change in δD_m (a measured delta value relative to the machine standard) with the overall equilibration period (the homogenization time plus additional 1 min). The δD_m values increase with time and

Fig. 3. (a) Reproducibility of δD_m value of the MSA-6 laboratory reference water prepared consecutively with the on-line chromium reduction method. (b) Change in δD_m of MSA-6 as a function of Cr number, the run number after a new batch of Cr was in use.

eventually reach a steady value after 6 min within an analytical error of 0.5‰.

Life of chromium Donnelly *et al.* (2001) state that approximately 180 runs are possible using 1 μ l of water per run in a reactor containing Cr of a similar amount and grain size. In our case, we found that 100~150 runs are possible using 2 μ l of water per run. Thus, our Cr consumption rate is better than that in Donnelly *et al.* (2001), reflecting effectiveness of the use of quartz glass sand. Much longer life of Cr has been reported by Nelson and Dettman (2001) who used Cr powder of finer grain sizes.

We found that several initial runs gave very low δD_m values immediately after changing to new Cr, probably reflecting “washing out” of surface contaminants during the initial runs. The life of Cr can be easily identified when the pressure transducer readings are lowered indicating the deterioration of the reduction capability of Cr. After the end of Cr life is reached, the resulting chromium oxide that is semi-consolidated inside the quartz glass tube can be removed by drilling with a long drill.

Fig. 4. The δD_m values of MSA-6 of various salinity.

Fig. 5. Consecutive δD_m measurements of the reference waters V-SMOW, SLAP, GISP and MSA-6. Memory effects are obvious after runs of a sample with a greatly different δD value. Number of flush runs is bracketed before the runs marked by solid circles.

Reproducibility and accuracy of analysis

Reproducibility The reproducibility of the δD measurement was checked using MSA-6, which is our laboratory water standard. Forty four replicate analyses of MSA-6 gave the average δD_m value (expressed relative to the machine reference H_2 gas) of 18.5 ± 0.5 (1σ)‰ (Fig. 3(a)). This reproducibility is satisfactory when compared to that obtained by conventional U reduction method (0.5‰), Zn method (0.4–0.8‰, Coleman *et al.*, 1982; Vennemann and O’Neil, 1993; Noto and Kusakabe, 1995), and is slightly better than the reproducibility by the H_2 - H_2O equilibration technique (0.5–1.4‰, Ohsumi and Fujino, 1986; Ohba and Hirabayashi, 1996). Satisfactory reproducibility was also obtained during the entire life of Cr as shown in Fig. 3(b). In this experiment MSA-6 was repeatedly measured from the beginning to end for a batch of Cr. No systematic change in δD_m value was observed as a func-

Fig. 6. Number of flush runs required to obtain 0.5‰ reproducibility as a function of the difference in δD_m values between previous and subsequent runs.

tion of the “Cr number” which was defined as the number of runs after a new batch of Cr was in use. The average δD_m value of 19.2‰ in Fig. 3(b) was slightly higher than that in Fig. 3(a) (18.5‰), suggesting that the performance of Cr used may be slightly different from a batch to batch depending on the Cr to quartz glass sand ratio and their homogeneity. It is recommended to run a laboratory reference water from time to time to secure the accuracy of δD measurement.

Salt effects The effect of salt dissolved in sample water on δD_m values was evaluated using MSA-6. Sodium chloride was added to MSA-6 reference water to obtain solutions of 500 to 10,000 ppm NaCl. The results are shown in Fig. 4. No systematic variation was observed, although a scatter of data greater than the typical reproducibility (± 0.5 ‰) was recognized in some cases. It has been known that deuterium is enriched in vapor in equilibrium with salt solution relative to pure water (Horita *et al.*, 1993; Kakiuchi, 1994). Most of the water was considered to evaporate quickly in the region between the syringe needle and Swagelok connector when the solution was injected into the Cr reactor (Fig. 1(b)). However, the salt effect due to progressive enrichment of salt during evaporation was unlikely from the mass balance consideration. It is difficult to quantify the degree of D enrichment as a function of salinity because the amount of water left as “brine” cannot be estimated. Considering a poorer reproducibility of δD value, replicate analysis is recommended for salt solutions.

Memory effect Memory effects have been clearly observed in Cr reduction methods (Gehre *et al.*, 1996; Donnelly *et al.*, 2001; Nelson and Dettman, 2001). In our system, memory effects are also observed as illustrated in Fig. 5. Replicate analyses are shown for VSMOW, SLAP, GISP (the international reference water samples distributed under the Analytical Quality Control Services program by IAEA) and MSA-6. The memory effects be-

Table 1. “Memory-free” δD_m values of V-SMOW, GISP, SLAP and MSA-6 reference waters

	V-SMOW	GISP	SLAP	MSA-6
	66.0	-127.8	-375.7	18.0
	66.8	-128.1	-375.8	19.1
	66.2	-128.9	-375.6	18.4
	67.2		-374.2	18.8
			-374.4	18.7
Average	66.5	-128.3	-375.1	18.4
1 sigma	0.5	0.6	0.8	0.5

The values are expressed in ‰ relative to the machine reference H_2 .

come smaller by repeating several runs of a sample following the runs of a previous sample that has a vastly different isotopic composition. The number of runs required for a sample to recover its own value within a reproducibility of 0.5‰ increases until a plateau is reached (Fig. 6). It is here that the memory effects due to a previous sample disappears. We found that 5 flush runs are required to obtain a satisfactory result when the difference in δD_m values between the previous and subsequent samples exceeds 350‰, 3 runs for the difference of $>\sim 150$ ‰, and 1 run for the difference of ~ 50 ‰. Rinsing the micro syringe several times before analyzing the next sample must be done if the same syringe is to be used again.

Table 1 lists the analytical results for the reference water samples that were considered to have no memory effects. Based on the “memory-free” δD_m values shown in Table 1, we can express the D/H ratio of any water sample in terms of δD relative to V-SMOW using a V-SMOW-SLAP scaling factor f as follows,

$$f_{\text{VSMOW-SLAP}} = (\delta D_{\text{VSMOW}} - \delta D_{\text{SLAP}}) / (\delta D_{\text{m(VSMOW)}} - \delta D_{\text{m(SLAP)}})$$

where $\delta D_{\text{VSMOW}} - \delta D_{\text{SLAP}} = -428$ ‰ is recommended (Gonfiantini, 1978).

CONCLUSIONS

Some practical aspects of an on-line chromium reduction method for D/H analysis of natural water have been proposed. With this method, D/H variations of natural waters can be analyzed accurately and efficiently if attention is paid to the reaction period, isotopic equilibration of H_2 gas between preparation system and an inlet variable volume of the mass spectrometer, salt effects and memory effects. The advantage of the method is easy operation, high efficiency and, high precision and accu-

racy. The on-line Cr reduction system is easily attached to a conventional, dual inlet IRMS at low cost.

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REFERENCES

- Bigeleisen, J., Perlman, M. L. and Prosser, H. C. (1952) Conversion of hydrogenic materials to hydrogen for isotopic analysis. *Anal. Chem.* **24**, 1356–1357.
- Coleman, M. L., Shepherd, T. J., Durnham, J. J., Rouse, J. E. and Moore, G. R. (1982) Reduction of water with zinc for hydrogen isotope analysis. *Anal. Chem.* **54**, 993–995.
- Donnelly, T., Waldron, S., Tait, A., Dougans, J. and Bearhop, S. (2001) Hydrogen isotope analysis of natural abundance and deuterium-enriched waters by reduction over chromium on-line to a dynamic dual inlet isotope-ratio mass spectrometer. *Rapid Commun. Mass Spec.* **15**, 1297–1303.
- Finnigan MAT (1997) The H/Device, a novel peripheral for measurement of D/H from microliter samples of water and organic molecules. Application Flash Report No. G27.
- Florkowski, T. (1985) Sample preparation for hydrogen isotope analysis by mass spectrometry. *Int. J. Appl. Radiat. Isot.* **36**, 991–992.
- Gehre, M., Hoefling, R., Kowski, P. and Strauch, G. (1996) Sample preparation device for quantitative hydrogen isotope analysis using chromium metal. *Anal. Chem.* **68**, 4414–4417.
- Gonfiantini, R. (1978) Standards for stable isotope measurements in natural compounds. *Nature* **271**, 534–536.
- Hayes, J. M. and Johnson, M. W. (1988) Reagent and procedure for preparation of H_2 for hydrogen isotopic analysis of water. Indiana University, Biogeochemical Laboratories, internal report.
- Horita, J. (1988) Hydrogen isotopic analysis of natural waters using a H_2 -water equilibration method: A special implication to brines. *Chem. Geol.* **72**, 89–94.
- Horita, J., Wesolowski, D. J. and Cole, D. R. (1993) The activity-composition relationship of oxygen and hydrogen isotopes in aqueous salt solutions: I. Vapor-liquid equilibration of single salt solutions from 50 to 100°C. *Geochim. Cosmochim. Acta* **57**, 2797–2817.
- Kakiuchi, M. (1994) Temperature dependence of fractionation of hydrogen isotopes in aqueous sodium chloride solutions. *J. Solution Chem.* **23**, 1073–1087.
- Kendall, C. and Coplen, T. B. (1985) Multisample conversion of water to hydrogen by zinc for stable isotope determination. *Anal. Chem.* **57**, 1437–1440.
- Morrison, J., Brockwell, T., Merren, T., Fourel, F. and Philips, A. M. (2001) On-line high-precision stable hydrogen isotopic analyses on nanoliter water samples. *Anal. Chem.* **73**, 3570–3575.

- Nelson, S. T. and Dettman, D. (2001) Improving hydrogen isotope ratio measurements for on-line chromium reduction systems. *Rapid Commun. Mass Spec.* **15**, 2301–2306.
- Noto, M. and Kusakabe, M. (1995) Reactivity of zinc for hydrogen isotope analysis. *Tech. Rep. ISEI* **B14**, 1–12 (in Japanese).
- Ohba, T. and Hirabayashi, J. (1996) Handling of Pt catalyst in H₂-H₂O equilibration method for D/H measurement of water. *Geochem. J.* **30**, 373–377.
- Ohsumi, T. and Fujino, H. (1986) Isotope exchange technique for preparation of hydrogen gas in mass spectrometric D/H analysis of natural waters. *Anal. Sci.* **2**, 489–490.
- Tanweer, A. (1990) Importance of clean metallic zinc for hydrogen isotope analysis. *Anal. Chem.* **62**, 2158–2160.
- Tanweer, A. and Han, L. F. (1996) Reduction of micro liter amounts of water with manganese for D/H isotopic ratio measurements by mass spectrometry. *Isotopes Environ. Health Stud.* **32**, 97–103.
- Vaughn, V. H., White, J. W. C., Delmotte, M., Troiler, M., Cattani, O. and Stievenard, M. (1998) An automated system for hydrogen isotope analysis of water. *Chem. Geol.* **152**, 309–319.
- Vennemann, T. W. and O'Neil, J. R. (1993) A simple and inexpensive method of hydrogen isotope and water analyses of minerals and rocks based on zinc reagent. *Chem. Geol.* **103**, 227–234.