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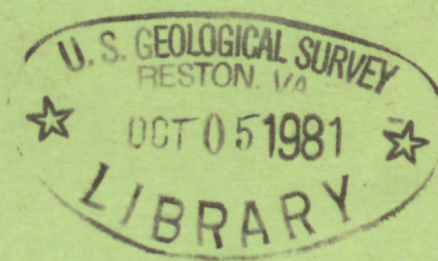
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MULTI-SALINE SAMPLE DISTILLATION APPARATUS
FOR HYDROGEN ISOTOPE ANALYSES:
DESIGN AND ACCURACY



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By AFIFA AFIFI HASSAN

ILLUSTRATIONS

Page

Figure 1. Sketch showing multi-saline sample distillation apparatus for hydrogen isotope analysis. 2



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CONTENTS

	Page
Abstract	1
Introduction	1
Apparatus	3
Method and Results	3,4
Conclusions	4
References	4

ILLUSTRATIONS

	Page
Figure 1: Sketch showing multi-saline sample distillation apparatus for hydrogen isotope analyses	2

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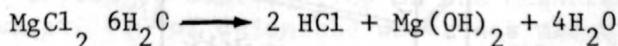
ABSTRACT

A distillation apparatus for saline water samples was designed and tested. Six samples may be distilled simultaneously. The temperature was maintained at 400°C to ensure complete dehydration of the precipitating salts. Consequently, the error in the measured ratio of stable hydrogen isotopes resulting from incomplete dehydration of hydrated salts during distillation was eliminated.

INTRODUCTION

The most commonly used method to convert water to hydrogen, for stable isotope analyses, is the reaction with hot uranium (Bigeleisen and others, 1952). However, water samples containing more than 1000 ppm salts require distillation before they are injected into the sample preparation vacuum line to minimize memory effects resulting from precipitation of dehydrated salts. Distillation vials containing glass beads (fig. 1) are used to distill water samples one at a time without a heat controller (Truesdell, personal oral communication to Tyler Coplen, 1978). The temperature is unknown.

The problem of concern is that upon evaporation, during distillation, hydrated salts that precipitate may not be completely dehydrated. For example, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Bischofite), $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Carnallite), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Epsomite), and $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ (Kieserite) may precipitate. To determine the hydrogen isotopic composition of the water accurately, all the water and OH groups must be driven out of these salts. Most of the water-containing salts, except Bischofite, completely dehydrate at 200°C or less. Bischofite dehydrates in two steps. The first step may form Brucite, $\text{Mg}(\text{OH})_2$, which in turn, dehydrates at 350°C. Another problem of concern is the loss of HCl formed during dehydration of the magnesium chloride salts. An example of the reaction is as follows:



Bischofite

Brucite

Single distillation of water samples also is time consuming. Accordingly, an apparatus suitable for distilling several saline samples simultaneously is needed. The apparatus should contain a heat controller to ensure that the temperature required to dehydrate Brucite, 350°C, is reached.

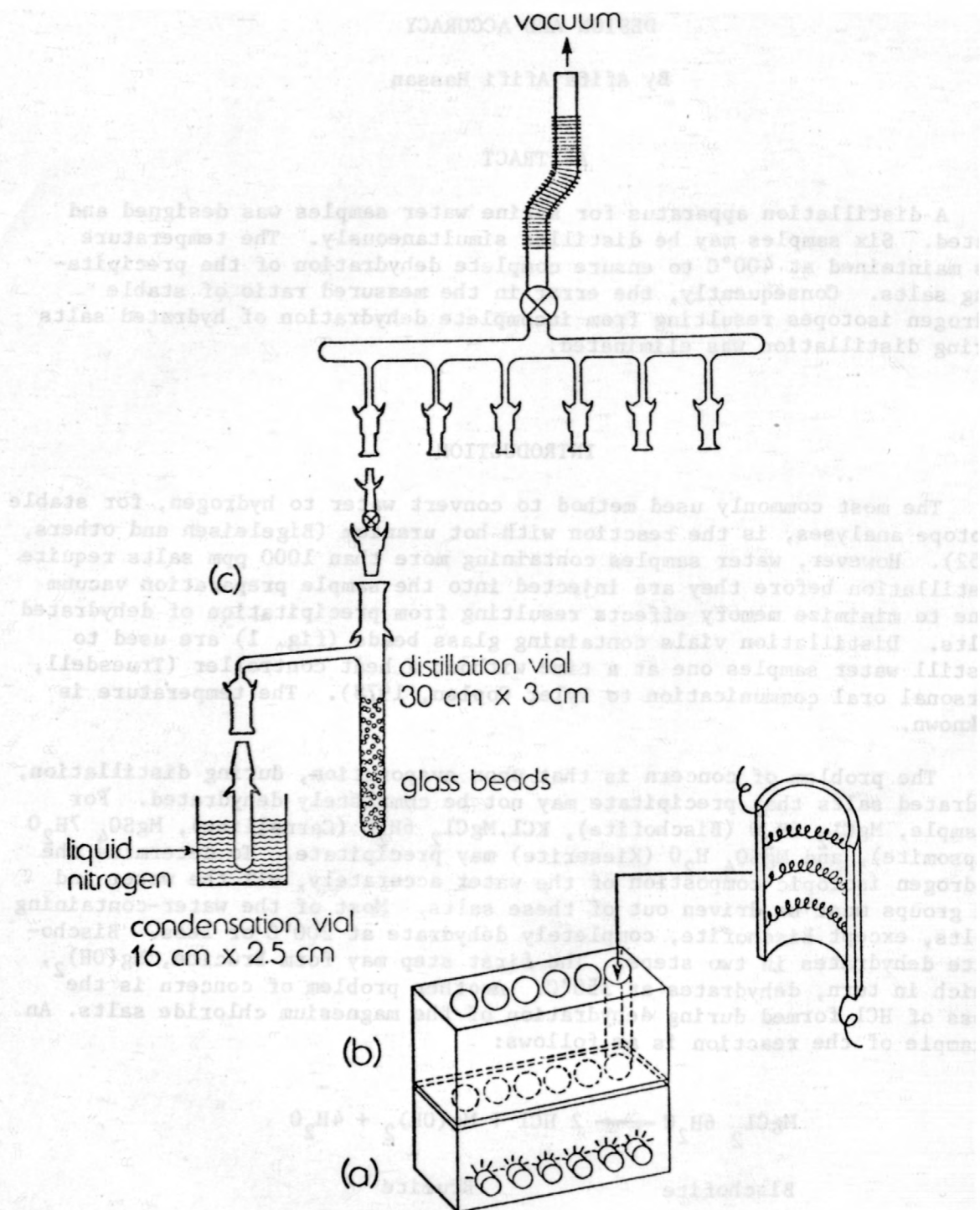


Figure 1: Multi-saline sample distillation apparatus for hydrogen isotope analyses (not to scale),

- (a) Micro-Kjeldahl apparatus with six individual heat controls.
- (b) Six heating elements, two half-shells each, enclosed in a heat-insulating box and connected to a variable auto transformer
- (c) Glass manifold connected to a vacuum line and distillation-condensation vials,

The apparatus in figure 1, as designed, consists of a micro-Kjeldahl apparatus with six recesses equipped with individual heat controls (fig. 1a). Another six heating units, each consisting of two half-shell heating elements, were built on top of the six recesses (fig. 1b). The heating elements were enclosed in a box of heat-insulating material and connected to a variable autotransformer to control the temperature. The variable autotransformer and the heat controls are calibrated to maintain the temperature at the top of the upper heating elements at 400°C and, at the bottom of the recesses, at 350°C.

A glass manifold with six ports and flexi-metal tube was designed to permit connection of the distillation apparatus to a vacuum line (fig. 1c). The ports were spaced so that two-thirds of the length of the distillation vials fit inside the heating elements with their bottom in the recesses of the micro-Kjeldahl apparatus. Each distillation vial has an arm, longer than the width of the distillation apparatus, connected to a condensation vial (fig. 1c).

METHOD AND RESULTS

The distillation vials were filled up to two-thirds of their height with glass beads. A pipette was used to inject a 2-ml water sample into the bottom of each vial. Six small dewars filled with liquid nitrogen were placed so that the bottom of the distillation vials were barely immersed in liquid nitrogen. After at least 3 minutes and after ensuring that water samples were frozen, the vials were evacuated.

The dewars containing liquid nitrogen were removed, and the manifold-distillation unit was adjusted via the flexi-metal tube so that the vials containing samples were placed inside the designated recesses of the heating apparatus. The upper parts of the vials were heated to 400°C before the bottoms were heated in order to flash to steam completely any saline water splashed on the beads and walls of vial. The temperature was monitored for 15 minutes while the condensation vials were immersed in liquid nitrogen. After ensuring that distillation was completed, the condensation vials were removed, the frozen distilled water was thawed, and the distilled water samples were stored.

To test the effect of distillation on the measured hydrogen isotopic composition of water, δD of deionized water was measured before and after distillation. The composition of sea water (Borchert and Muir, 1964, p. 186) was simulated by dissolving H-free salts in deionized water of known δD . After distillation, δD of the prepared sea water was measured to detect the effect of presence of salts on the δD of the distilled water. Six samples of the deionized water and the prepared sea water were distilled. Two groups of samples were distilled to detect the variation due to the analytical procedure.

1/ δD SMOW per mil = $[(R \text{ sample} / R \text{ standard}) - 1] 1000$, where $R = D/H$ (Hydrogen mass-2/Hydrogen mass-1) and the standard is Standard Mean Ocean Water (SMOW).

Water samples of each group of distillates, deionized water and sea water, were converted to hydrogen by reaction with uranium at 800°C under vacuum. Two separate conversions of the same sample were done. The resulting gas was analyzed by a modified double-collector mass spectrometer. The measured δD of the deionized water before distillation was -44.5 per mil relative to SMOW. After distillation, the mean δD was -44.5 ± 0.6 and -44.4 ± 0.5 for the deionized water and the prepared sea water, respectively. These results indicate that the standard deviation of the analyses is less than one per mil, the accepted precision of the mass spectrometer, and also that the procedure of distillation at 400°C does not introduce error in the hydrogen isotopic composition of the saline water. An analysis of variance also shows no significant differences between results in the 5-percent probability level.

CONCLUSIONS

The apparatus is efficient because six water samples can be distilled simultaneously. The apparatus also distills sea water with no measureable isotopic fractionation. It seems that the HCl produced during dehydration of Bischofite reacts with other precipitates such as Na_2CO_3 . Accordingly, no error was detected in the present test.

The apparatus should also be satisfactory for distilling very saline brines because during these distillation experiments a stage was reached where the solution was very saline. Accordingly, a simulated brine water was not tested. However, the new apparatus has been used satisfactorily to distill the natural brine samples sent to the laboratory during the past year.

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