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A PROCESS FOR RECOVERING IODINE-129

H.A. O'Brien, Jr. and J.M. Sullivan

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ISOTOPES DEVELOPMENT CENTER

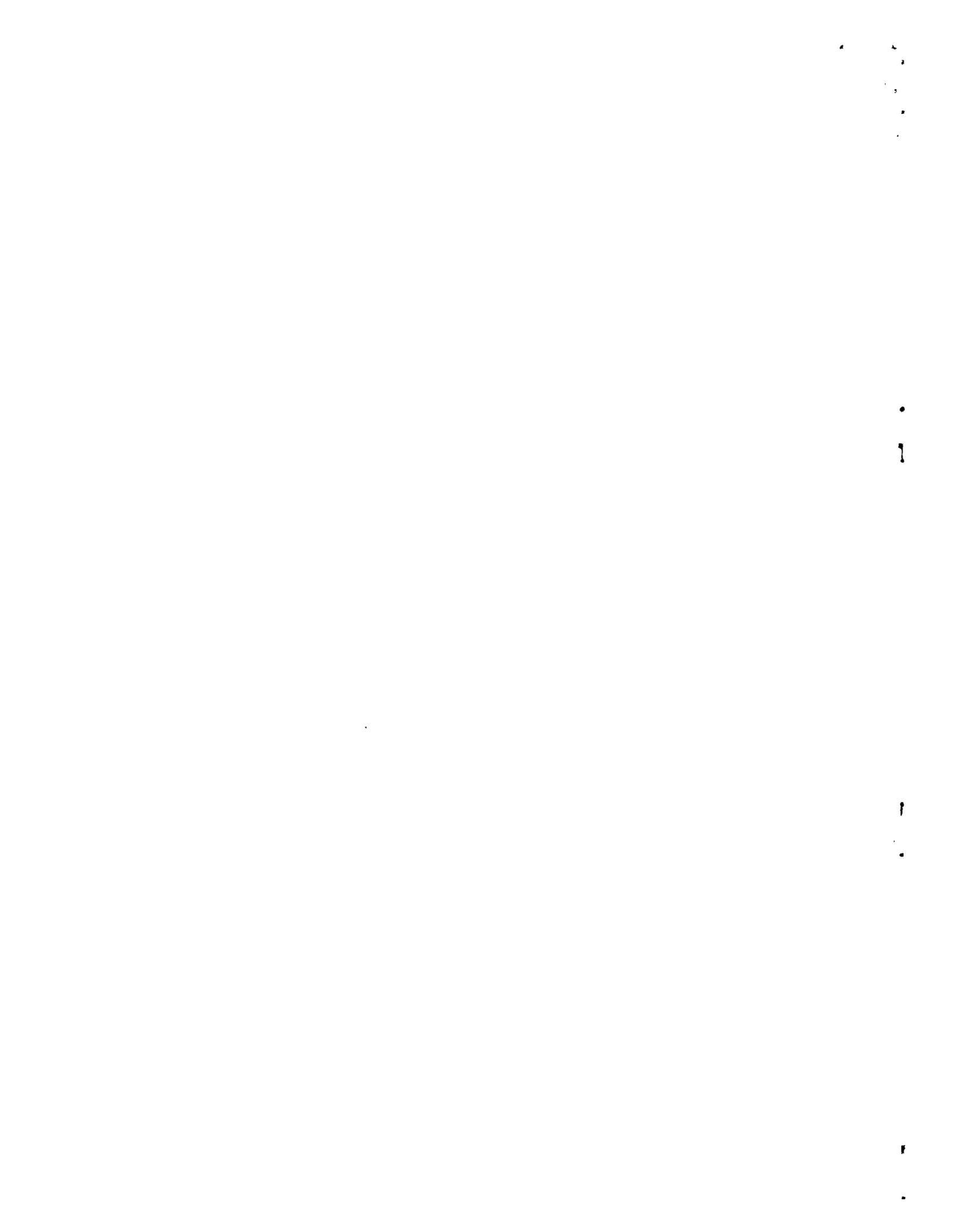
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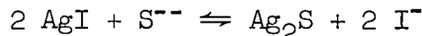
ABSTRACT

A process was developed on a laboratory scale for recovering, in 90-95% yield, I^{129} from Berl saddles impregnated with $AgNO_3$. The iodide ion is displaced from silver iodide by sulfide ion in alkaline solution, and I^{129} is distilled from the 1 M NaOH-0.01 M Na_2S solution after oxidation with hydrogen peroxide.

INTRODUCTION

During the processing of spent reactor fuel, I^{129} — a product of U^{235} fission — is released in elemental form upon dissolution of the uranium metal in nitric acid; it is then carried in the off-gases to a scrubbing tower containing Berl saddles impregnated with $AgNO_3$ where it is trapped as the highly insoluble AgI . Previously, the I^{129} has been recovered in 50% yield from the intact Berl saddles by reducing the silver with powdered zinc and oxidizing the iodide to iodine with nitric acid.¹ It is possible to increase recovery to nearly 90% by grinding the saddles to 100 mesh, but the hazard of handling the dry radioactive powder precludes the use of this modification.

The method presented here permits recovery of I^{129} in 90-95% yield and is based on the displacement of the iodide from the AgI by sulfide ions present in an alkaline solution. Limited previous work has involved the study of the $AgI-Ag_2S$ equilibrium in acid media.^{2,3} Alkali has the advantages of reducing the hydrolysis of the sulfide ion and increasing the sulfide ion concentration, thereby shifting the equilibrium



to the right.

¹H. T. Russell, Recovery and Half-Life Determination of I^{129} , ORNL-2293 (May 1957).

²A. A. Noyes and E. A. Freed, J. Am. Chem. Soc. 42, 476 (1920).

³I. M. Karenman, J. Gen. Chem. (USSR) 16, 165 (1946).

Since the solubility product constant of AgI is 10^{-17} but that of Ag_2S only 10^{-51} , iodide ion is essentially totally released. The caustic also increases the porosity of the ceramic saddles and exposes additional silver iodide trapped near the surface.

The procedure was developed on a laboratory scale but has more recently been adapted to a production scale.

PROCEDURE

Removal of Iodine from Berl Saddles

The saddles containing the AgI, in 50-g lots, are washed twice with 200-ml portions of boiling water to remove as much silver nitrate as possible and then are soaked 24 hrs in 250 ml of a solution 1 M in NaOH and 0.01 M in Na_2S . The supernatant liquid is filtered to remove the precipitated silver sulfide.

These concentrations of NaOH and Na_2S were selected for the leaching solution after preliminary tests showed that increasing the sulfide above this value had little effect on the iodine extraction (Table 1). However, decreasing the NaOH below this value decreased the sulfide ion concentration and resulted in less efficient iodine extraction.

Table 1. Effect of Sulfide and Hydroxyl Ion Concentrations on Removal of I^{129} from Berl Saddles

NaOH Concentration (M)	Na_2S Concentration (M)	I^{129} Removed (%)
1.0	0.1	95
	0.01	98
	0.001	68
	0.000	17
0.1	0.01	88
0.01	0.01	82

Recovery of Iodine from Alkaline Sulfide Solution

The filtrate from the above step is transferred to a 1-liter distillation flask supplied with a Snyder reflux column, as shown in Fig. 1, and the pH is adjusted to 1.0 with 3 N H_2SO_4 . (More concentrated acid should not be used because of the danger of oxidizing some iodide to iodine at this point and distilling it off in the preliminary hydrogen sulfide removal step. In the test work no iodine was ever detected in the vapor when the pH was kept at 1.) The elemental sulfur that forms does not hinder the subsequent steps. This solution is refluxed until the evolution of H_2S ceases, as shown by a test with lead acetate paper

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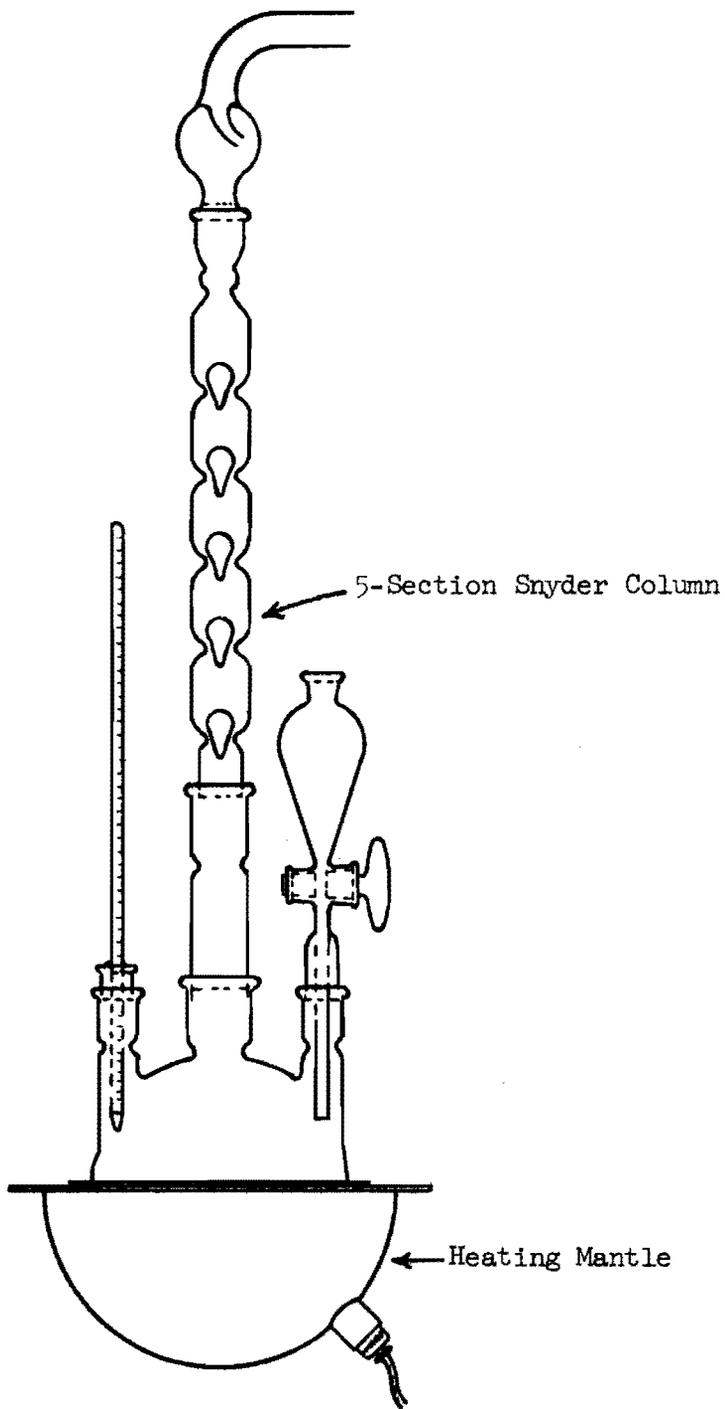


Fig. 1. Reflux System for Removal of H₂S.

at the top of the condenser -- usually 20 to 30 min. To reduce any iodate still present, approximately 5 ml of 0.2 M NaHSO_3 is added through the addition funnel.

The complete distillation apparatus is now assembled (Fig. 2), and 10 ml of 0.2 M NaHSO_3 is added to the scrubber. The iodide is oxidized to iodine with 20 ml of 10% H_2O_2 containing 5 drops of 3% ammonium molybdate as catalyst⁴ -- again added through the addition funnel -- and the solution is boiled until visible evolution of iodine ceases. The liquid is then cooled and the oxidation and distillation steps are repeated until the absence of iodine in the solution is shown by the absence of any brown tinge.

Sampling and Analysis

Material balances are obtained by determining the I^{129} in the unused saddles, in the saddles that have been processed, and in the scrubber solution. Three saddles of each type, randomly selected, are ground to a fine powder, and about 0.1 g of each powder is weighed and mounted on a standard 3.75- by 2.5-in. one-hole laminated beta mounting card. A 250- λ aliquot of the scrubber solution is evaporated to dryness on a 1-in.-dia glass disk, which is mounted on a similar card. The height of the 39-kev I^{129} gamma peak of each sample is determined with a Nuclear Data 256-channel analyzer. The resolution of this instrument is 7% as measured by the FWHM of the 0.663-Mev Cs^{137} gamma peak.

CONCLUSION

The procedure described is suitable for efficient recovery of I^{129} and has been adapted to large-scale operations. For example, a 50-liter stainless steel tank with suitable filter can be installed at the processing site. The saddles, after being placed in a coarse mesh bag, can be immersed in the caustic-sulfide solution and allowed to remain there for 24 hrs. This batch can then be removed and replaced with another, and the sulfide solution drawn off and processed as required.

⁴I. M. Kolthoff and E. B. Sandell, Textbook of Quantitative Inorganic Analysis, Macmillan Co., N. Y., 1952, p. 33.

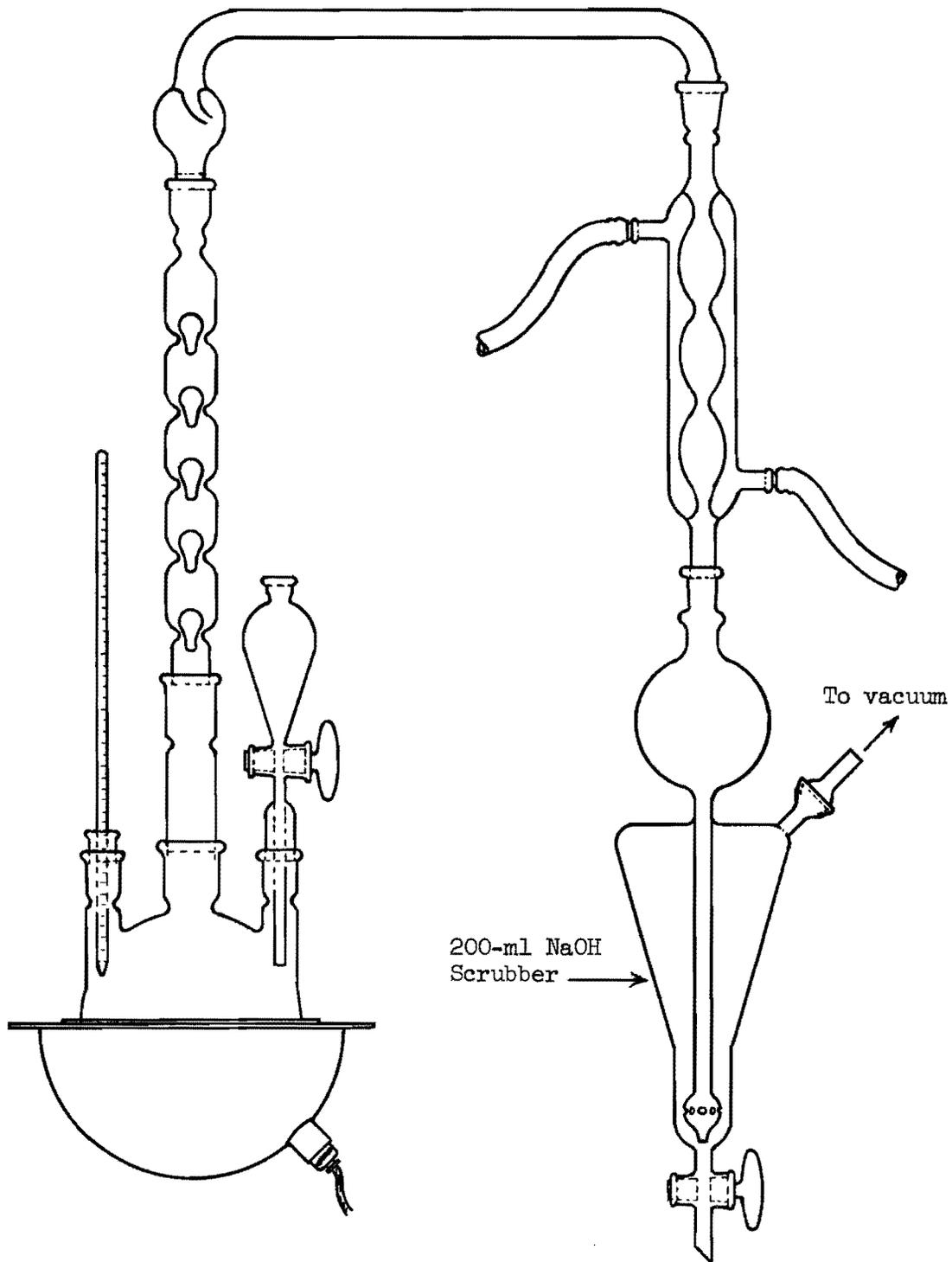


Fig. 2. Apparatus for Recovery and Distillation of Iodine.



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