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DETERMINATION OF HEAVY WATER PURITY
BY INFRARED ABSORPTION

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A B S T R A C T

The practical application of heavy water purity determination by infrared absorption spectroscopy using standard laboratory equipment has been demonstrated in connection with the operation of heavy water moderated Special Power Excursion Reactor Test (SPERT II) Facility at the NRTS.

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INTRODUCTION

It is necessary to know the heavy water moderator purity within 0.05 mole per cent in the Special Power Excursion Reactor Test (SPERT II) Facility at the NRTS in order to evaluate and to duplicate reactor performance. Further, accountability for \$2,000,000 worth of material requires accurate knowledge of quantity and purity of various portions of rinse water, storage tank contents, spill salvage and reserve stock supplies as well as the reactor water.

The first analyses were made by the density method, which is absolute, provided O^{18} is known, and does not require an involved calibration procedure. However, the density method does require meticulous handling and very precise weighing. When samples are received irregularly in a laboratory that must handle a wide variety of analyses and cannot keep personnel and equipment ready for a particular operation, the time required to do an isotopic purity analysis by density measurement becomes excessive. The infrared method was investigated and developed to provide a rapid, precise analysis over the purity range that included most of the samples expected to be submitted.

APPARATUS USED

1. Perkin-Elmer Model 21, Infrared Spectrophotometer, with NaCl prism, operated with a source current of 0.35 amperes and the slit program at 960, giving a slit opening of about 30 microns at the analytical wavelength of 2.95 microns.
2. Standard Perkin-Elmer sealed absorption cells equipped with fused silica windows and lead spacers.
3. Hypodermic syringes, 10 ml. capacity.
4. Dry box.

CALIBRATION

Calibration mixtures were prepared from a drum of the original shipment of reactor water. Density measurements made at the CPP agreed with the suppliers' analysis of 99.77 mole per cent pure. This value was accepted as correct. The mixtures were prepared by pipetting 1, 2, 3, 4, and 5 ml. of distilled water into 500 ml. portions of the standard material. It is believed that the dilutions, which were carried out in a dry box, were accurate within 0.01 mole per cent absolute.

The original calibration data were obtained according to a program designed by the Mathematical Statistical Group to indicate precision and residual effects while providing a calibration curve. Each standard was run following each of the others. A cell blank was run with each series of six calibration runs. The cell was dried by evacuation and its transmission recorded over the range of about 2.7 to 3.1 microns. The 100% adjusting comb in the sample beam was withdrawn to compensate in part for the absorption of the quartz windows. The cell was filled in a dry box which was kept dry with Linde Molecular Sieve. Four hypodermic syringes of 10 ml. capacity were used for filling the cell. These were kept in a drying oven at 100°C. until just before being used. Each was used once and returned to the oven. Five ml. of standard were drawn into the syringe and pushed through the cell, serving as a rinse. The last portion remaining in the cell was retained as sample. Between runs, the filling ports of the cell were dried with kleenex. This usually drew the sample from the absorbing path as well, but no further attempt was made to dry the cell.

Later calibration procedures were the same except that 3 ml. aliquots of sample were used. It was shown that 1 ml., which represents approximately ten changes in the cell, was sufficient to replace the previous sample, but that it sometimes failed to remove the bubbles from the absorbing path. Figure 1 shows a typical recording of a calibration series using a 150 μ cell. The absolute transmission of the empty cell is shown here for illustration, although it was usually not recorded. The 2.75 μ absorption band of quartz and the interference fringes of the empty cell are visible. At the top is the transmission of the empty cell with the 100% comb withdrawn. This is used as I_0 . The other traces are those of the three "standards" indicated. The statisticians fitted an equation to the data and calculated additional points. The resulting curve is shown in Figure 2. The standard deviation of a single determination in this concentration range was calculated to be 0.0024 mole % D_2O . This is the method currently being used for the majority of the analyses. In the case of materials of slightly lower purity, such as rinse water, a slightly shorter cell path is used. Figure 3 shows the calibration curve obtained for a cell with a nominal 100 μ path length. The standard deviation for a single determination using this cell and in this range is 0.0042 mole % D_2O .

ANALYTICAL PROCEDURE

Samples for analysis are taken in polyethylene bottles holding about 150 ml. The bottles are used as received, without rinsing or drying. The bottles are filled completely and capped with open-topped plastic caps having neoprene disc inserts, available from Formold Plastics, Inc., 11955 Vincennes Avenue, Blue Island, Illinois. Samples taken in this way can be transported without fear of breakage and can stand in the atmosphere for at least a week without measureable loss of purity. A portion of the sample is withdrawn through the neoprene disk with a hypodermic syringe without removing the cap. Although the entire cell filling operation can be carried out in the atmosphere, the operation must be done in the dry box if the rinsings are to be salvaged. It has been found necessary to use a dry syringe, just removed from the oven, for each filling. Once the cell was filled and plugged, the absorbance remained constant for at least two hours.

DISCUSSION

The observations of this laboratory concerning handling of heavy water samples in general are in agreement with those of Gaunt at Harwell, as reported in AERE C/R 1264, with two exceptions. Difficulty was reported in keeping small samples, even in a dry box. At CPP, a 400 ml. sample of 99.77% D_2O used as a secondary standard was kept in a screw-cap glass bottle in a dry box and opened about once a week for nine months with a loss in purity of less than 0.01%. Gaunt described a method of drying the absorption cell by rinsing with acetone, blowing out and drying in a desiccator for several hours. It has been found much more convenient to use a vacuum pump. Distilled water is removed to give a reproducible cell blank in 2 to 3 minutes.

The utility of infrared spectrometry in the operation of a heavy water moderated reactor has been demonstrated during a year's use at the NRTS. The instrument can be used for other work and be ready for heavy water on a minute's notice. It can be reset to wavelength, the cell blank recorded, and five samples recorded, calculated and reported in 40 minutes, for an average of 8 minutes per sample even when the cell is filled in the dry box. Data on duplicate samples have verified in practice the 95% confidence level of 0.005 mole per cent which was predicted from the calibration data. The rapidity and precision of the method have permitted a more complete inventory and a better evaluation of reactor performance than could have been approached by any other analytical method available in the area.

Figure 1

CALIBRATION SCANS WITH
150 MICRON CELL.

Figure 2

CALIBRATION CURVE FOR
150 MICRON CELL.

CPP-S-2021

Figure 3

CALIBRATION CURVE FOR
100 MICRON CELL.

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