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A CRYSTAL MICROBALANCE FOR DETERMINATION
OF OIL IN WATER

James V. Mengenhauser

Army Mobility Equipment Research and
Development Center
Fort Belvoir, Virginia

May 1973

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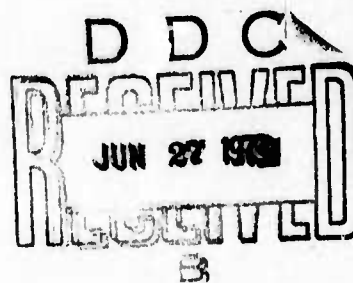
Report 2057

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by

Dr. James V. Mengenhauser

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SUMMARY

Evaluation tests were performed on the Esso crystal microbalance to determine its suitability as a means of determining trace amounts of oil in water. Aliquots of methylene chloride used to extract the oil from the water were allowed to evaporate on one of the two balance crystals, causing a change in the beat frequency proportional to the mass of the oil. The constant relating mass and beat frequency was found to be approximately 4.3×10^{-10} gram/Hz. The standard deviation of replicate aliquots of the same sample did not exceed 2 percent of the mean in the 3000- to 7000-Hz range. Standardization curves were prepared for the determination of No. 2 diesel fuel and Navy Distillate in tap water at concentrations up to 200 ppm by volume and for the determination of mixed No. 2 diesel fuel/type 9250 lubricating oil (5:1 by volume) in tap water and in well water up to 100 ppm by volume.

FOREWORD

This research was conducted by the Fuels Surveillance and Technology Branch, Fuels Handling Equipment Division, Mechanical Technology Department, U. S. Army Mobility Equipment Research and Development Center, Fort Belvoir, Virginia.

The crystal microbalance evaluated in this report was furnished by the Esso Research and Engineering Company, Florham Park, New Jersey. The instrument was obtained by USAMERDC, at no cost to the Government, under R&D Release Document No. 2358.

The test and evaluation of the Esso crystal microbalance was part of a joint U. S. Coast Guard and U. S. Army Mobility Equipment Command program to evaluate the current state of the art covering oil/water separation, detection, and measuring equipment.

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A CRYSTAL MICROBALANCE FOR DETERMINATION OF OIL IN WATER

I. INTRODUCTION

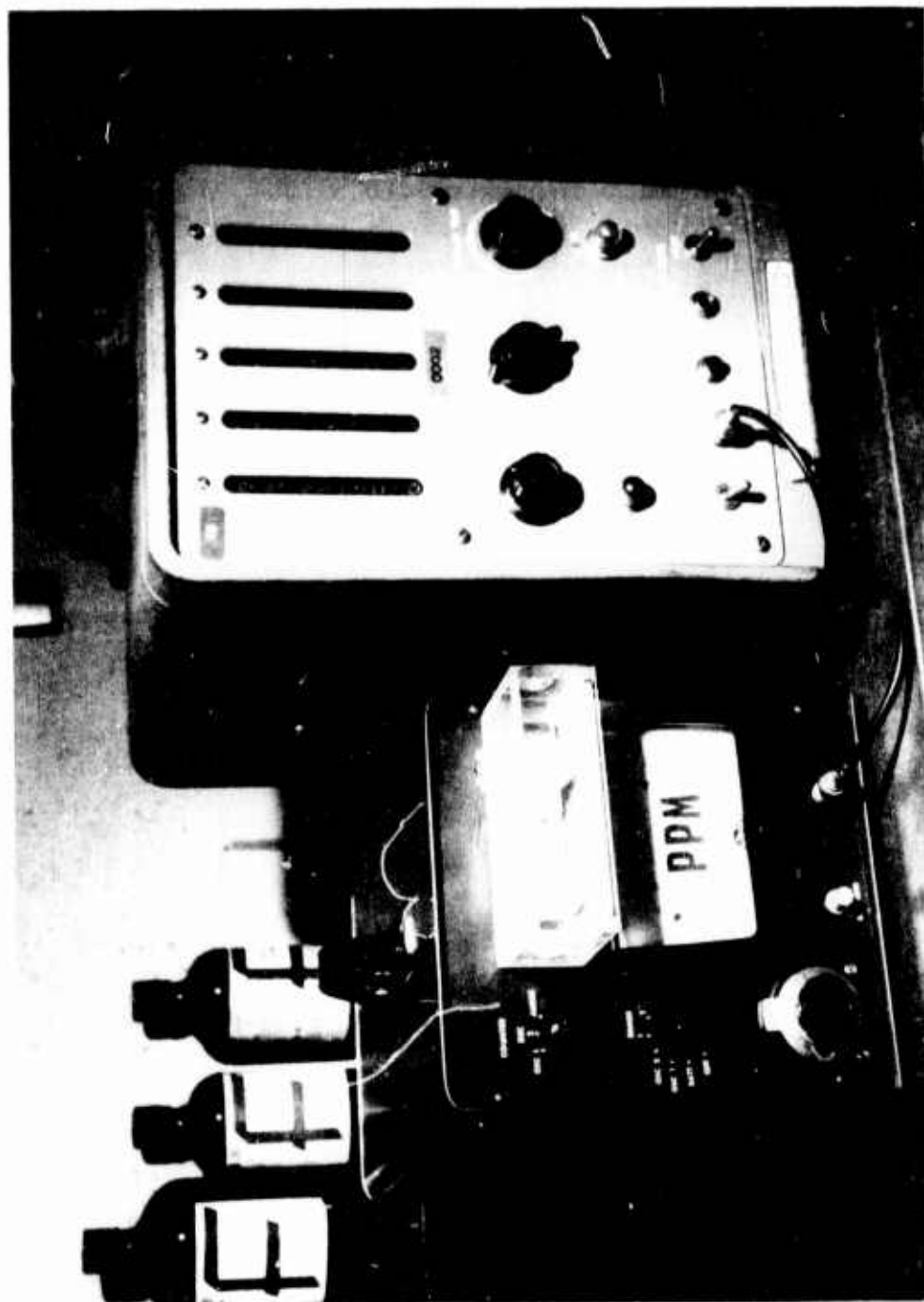
1. **Subject.** This report covers evaluation tests made on the Esso crystal microbalance for the purpose of determining trace amounts of oil in water. After suitable standardization with known concentrations of various oils, several hundred field samples from the effluent streams of oily water separators were run on the instrument to gain experience with the instrument as an analytical tool.

2. **Description and Operation of the Instrument.** The instrument consists of a control panel, meter, circuitry, and battery pack which powers two crystal oscillators about 1.5 cm in diameter. The beat frequency of the crystals can be read out on the self-contained meter or on an external frequency counter. A photograph of the instrument is shown as Fig. 1. The crystals are visible under the plastic cover, which protects the crystals from dust and drafts during operation.

The operation of the instrument is simple. First, both crystals are cleaned with solvent and allowed to dry. The beat frequency of the clean crystals is adjusted to zero. Next, a solvent extract of the oily water sample is placed on one crystal and allowed to evaporate. Finally, the beat frequency is again read after the solvent has evaporated. The beat frequency is proportional to the mass of the oil residue remaining.

II. INVESTIGATION

3. **Calibration.** The sensitivity of the instrument was determined by recording the beat frequency as a function of mass of the oil on the crystal. For these tests, solutions containing 706, 1000, and 1418 mg/l of vacuum pump oil in methylene chloride were prepared. Samples of 2.00 μ l volume were placed on the crystal with a 10- μ l Hamilton syringe. The average beat frequency observed for the 706-mg/l solution was 3360 Hz for 15 determinations. Since the mass of oil in 2.00 μ l of the 706-mg/l solution is 1.412 μ g, the sensitivity is 4.20×10^{-10} g/Hz. Similar determinations were made with the 1000- and 1418-mg/l solutions. The average sensitivities for 27 determinations were 4.25×10^{-10} g/Hz and 4.40×10^{-10} g/Hz for 2.00 μ l of the 1000 and 1418 mg/l solutions, respectively. These figures indicate a slight decrease in sensitivity as the oil load increases from 1.4 to 2.8 μ g. It is not known whether the change in sensitivity with mass is due to a nonlinear response of the crystal itself or whether a larger size "puddle" of oil causes less damping per unit mass than a small "puddle." Regardless of the cause,



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Fig. 1. The Eso crystal microbalance with plastic dust cover in place. The wire device near the handle attaches to the crystal to keep the solvent drop in place during evaporation.

however, the effect is small enough to be easily corrected by calibration. The sensitivity constant is probably different for each crystal, but this possibility was not explored. In any case, recalibration could be performed if the crystal was changed.

4. Reproducibility of the Method. Several sets of determinations were made on the same sample to evaluate the reproducibility of the method. In each case, the sample size was 2.00 μ l. The results are given in Table I. These figures indicate that a standard deviation of approximately 2 percent is a reasonable expectation over the range from 3000 to 7000 Hz. The standard deviations include the deviations due to the syringe as well as those from the instrument.

Table I. Reproducibility of Readings on the Crystal Microbalance

No. of Determinations	Mean Beat Frequency (Hz)	Standard Deviation (Hz)	Standard Deviation (%)
5*	3431	67	1.95
7	6611	107	1.62
5*	3395	68	2.00
5	4862	98	2.02

*The same solution was used in both sets of determinations, but different syringes were used.

Occasionally, readings were taken which were considerably higher or lower than the expected values. The low readings were sometimes due to the presence of air bubbles in the syringe and could be corrected by repeated flushing of the syringe. The spurious high readings could not be so easily rationalized. The most likely explanation is that they are caused by dust particles settling on the crystal while the dust cover is removed for insertion of the sample. From the sensitivity constant, it can be calculated that a 0.1- μ g dust particle would change the beat frequency by 240 Hz. In fact, a dust particle could cause the reading to be either high or low. If it landed on the sample crystal the beat frequency would increase, while a particle on the reference crystal would decrease the beat frequency. If the dust particle was heavier than the oil residue, the beat frequency would increase regardless of which crystal the dust particle landed on. It is recommended that duplicate readings be taken on all samples because of possible dust contamination. If the readings differ by more than two standard deviations, additional readings should be taken.

5. Determination of Navy Distillate. A standardization was next set to determine Navy Distillate in tap water samples from a test separator effluent. The standards were prepared by placing 50 ml of tap water in 100-ml sample bottles with foil-lined caps, adding Navy Distillate with a microliter syringe, and shaking for 30 minutes on a

mechanical shaker to thoroughly disperse the sample into the water. Twenty milliliters of reagent grade dichloromethane (CH_2Cl_2) were added to the water, and the mixture was shaken for another 15 minutes. Standards were prepared at concentrations of 0, 10, 20, 40, 60, 80, 100, 120, 140, 160, 180, and 200 μl of Navy Distillate per liter of tap water. Since the specific gravity of this fuel was 0.89, these concentrations range from 0 to 178 ppm by weight.

Samples of 2.00 μl were withdrawn from the CH_2Cl_2 layer and placed on the sample crystal of the microbalance. Readings were taken on the frequency counter exactly 3 minutes after the sample was inserted. The results are shown on Fig. 2. Each point represents the mean of two or three readings. The points are seen to form a straight line over the range covered.

From the sensitivity constant, it is possible to calculate the mass of oil recovered and compare it with the amount added to the sample. In the most concentrated sample, 10.0 μl (8.9 mg) of Navy Distillate was added to 50 ml of water, then extracted into 20-ml CH_2Cl_2 . If 100 percent extraction of the oil into the CH_2Cl_2 is assumed, the concentration of oil is 8.9 mg/20 ml, or 0.89 μg oil in a 2.00- μl sample of CH_2Cl_2 . The beat frequency for this sample, 1390 Hz, multiplied by the sensitivity constant, 4.20×10^{-10} g/Hz, equals 0.556 μg . Thus, the recovery of oil by this procedure is $0.556/0.89$ or 62 percent. The remaining 38 percent of the oil was lost due to incomplete extraction and evaporation loss of the light ends of the oil during the 3-minute waiting period before the beat frequency was read. Evaporation loss is believed to account for most of the non-recovered oil, but the actual source of the loss is unimportant since the standardization procedure compensates for it.

6. Determination of No. 2 Diesel Fuel. Another standardization curve was constructed to determine the presence of No. 2 diesel fuel in tap water effluent from oily water separators. Standards were prepared as in paragraph 3, except that No. 2 diesel fuel (specific gravity = 0.85) was used in place of Navy Distillate. The concentrations of fuel in the standards were 0, 50, 100, 150, and 200 μl fuel/liter tap water. The oil was then extracted by shaking with 10 ml CH_2Cl_2 for 15 minutes. As before, 2.00- μl aliquots of CH_2Cl_2 were placed on the sample crystal and allowed to evaporate for exactly 3 minutes prior to reading the beat frequency. The results are shown in Fig. 3. Each point represents the mean of two or more aliquots from the same sample. In contrast with the previous results with Navy Distillate, the beat frequency as a function of diesel fuel concentration was slightly non-linear. The reason for the non-linearity was not investigated further, but the volatility and solubility of the two fuels are different. Also, the extraction procedures were different; 10 ml CH_2Cl_2 and 70 ml water were used in the No. 2 diesel calibration, as compared with 20 ml CH_2Cl_2 and 50 ml water in the Navy Distillate procedure.

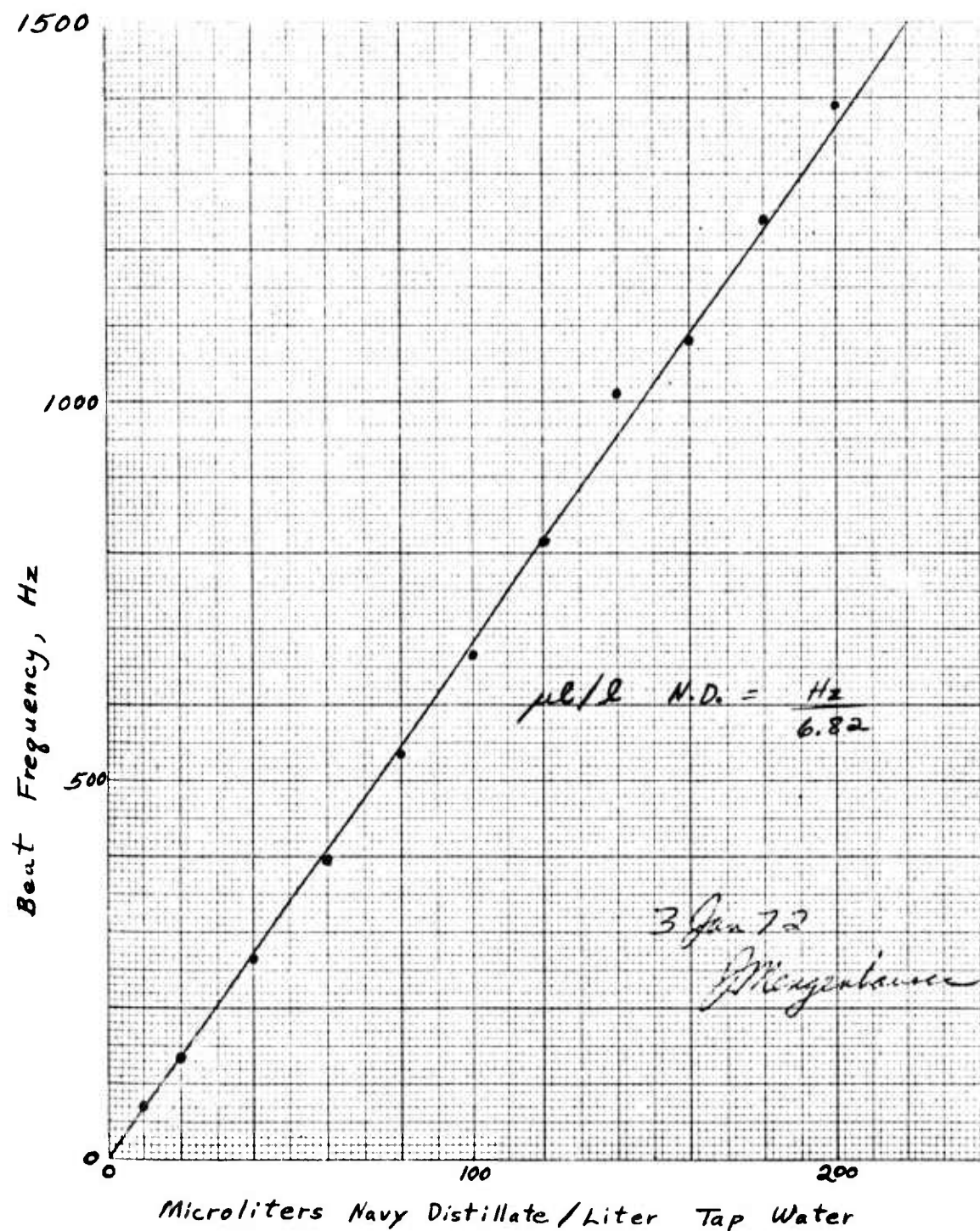


Fig. 2. Calibration for Navy Distillate in tap water. Fifty-milliliters water was shaken with 20-ml CH_2Cl_2 for 15 minutes. Beat frequencies were read after 3 minutes evaporation.

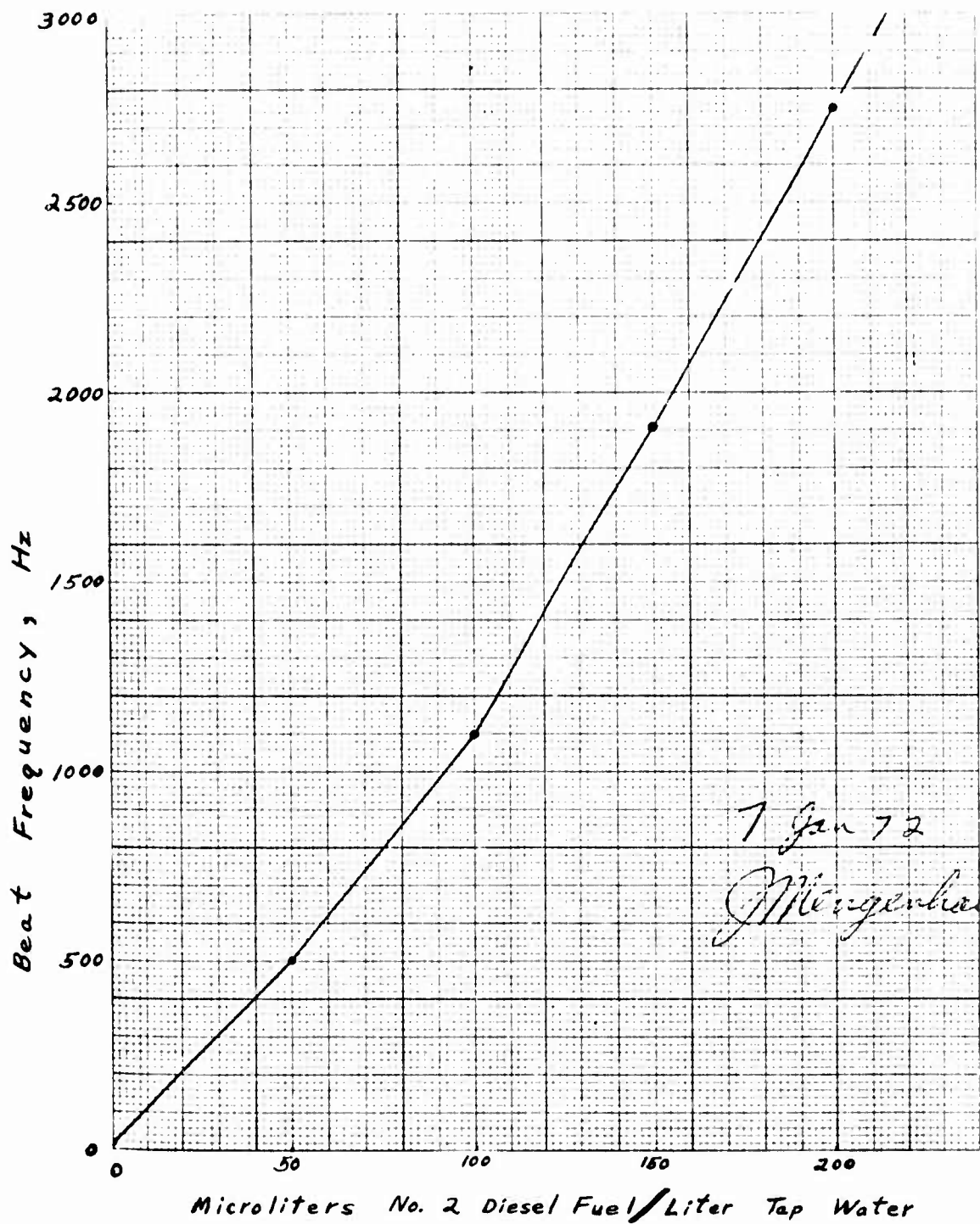


Fig. 3. Calibration curve for No. 2 diesel fuel in tap water. Seventy-milliliters water was shaken with 10-ml CH_2Cl_2 for 15 minutes. Beat frequencies were read after 3 minutes evaporation.

The amount of No. 2 diesel fuel recovered was calculated as before for the most concentrated sample. Assuming 100 percent extraction and neglecting the solubility of CH_2Cl_2 in water, a 2.00- μl aliquot of CH_2Cl_2 would contain 2.38 μg of diesel fuel. The amount recovered was calculated as 1.15 μg from the beat frequency and the sensitivity constant. The recovery percentage is thus 48 percent. Since No. 2 diesel fuel is more volatile than Navy Distillate, the lower recovery is to be expected. The recovery is not constant and decreases to 36 percent at low concentrations of diesel fuel.

7. Determination of No. 2 Diesel Fuel/Lubricating Oil Mixture. Since one of the potential applications of this instrument is to determine oil in bilge water, standardizations were carried out for a mixture of No. 2 diesel fuel and type 9250 lubricating oil (5:1 by volume) in water. This mixture was used to test oily water separators and is believed to be reasonably typical of what might be found in bilge water. Standardizations were made for the oil mixture in tap water and in water made up to a specific gravity of 1.023 with sea salt to simulate sea water.

Standards were prepared at concentrations of 0, 20, 40, 60, 80, and 100 μl of oil mixture per liter of tap water. A similar set was prepared in the simulated sea water to determine whether the additional salt content would affect the results. Samples containing 70 ml of water were extracted with 10 ml CH_2Cl_2 by shaking for 15 minutes on a mechanical shaker. Aliquots of 2.00 μl CH_2Cl_2 were withdrawn with a syringe and allowed to evaporate on the crystal for 3 minutes. Results are shown in Figs. 4 and 5. Each point represents the mean of three aliquots. The tap water data in Fig. 4 seem to fall on a slightly curved line, while the saltwater data in Fig. 5 fall on a straight line. When the experimental error is taken into account, there is little difference between the tap water and saltwater data. The scatter of the points in Fig. 4 was greater than those in Fig. 5. The data in Fig. 4 were taken on a hot day with the laboratory air conditioner in operation, causing the air temperature inside the laboratory to fluctuate over a 5° F range as the air conditioner compressor cycled on and off. On the other hand, the saltwater data in Fig. 5 were taken on a day when neither the air conditioner nor the heater was in operation, and the temperature remained constant. It is therefore recommended that, if possible, the instrument be operated in a constant temperature environment for best results.

At the highest concentration, 100 μl of oil per liter of water, the lines in both Figs. 4 and 5 are intersected at approximately 1430 Hz. The recovery, calculated as before, is 50 percent. This compares to a recovery of 39 percent for No. 2 diesel fuel alone at the same concentration. The higher recovery for the mixed oil is due to the presence of non-volatile lubricating oil in the mixture.

8. Miscellaneous Tests. Attempts to set up a calibration curve for JP-5 were unsuccessful due to the high volatility of the fuel. It was found that 96 percent of the JP-5

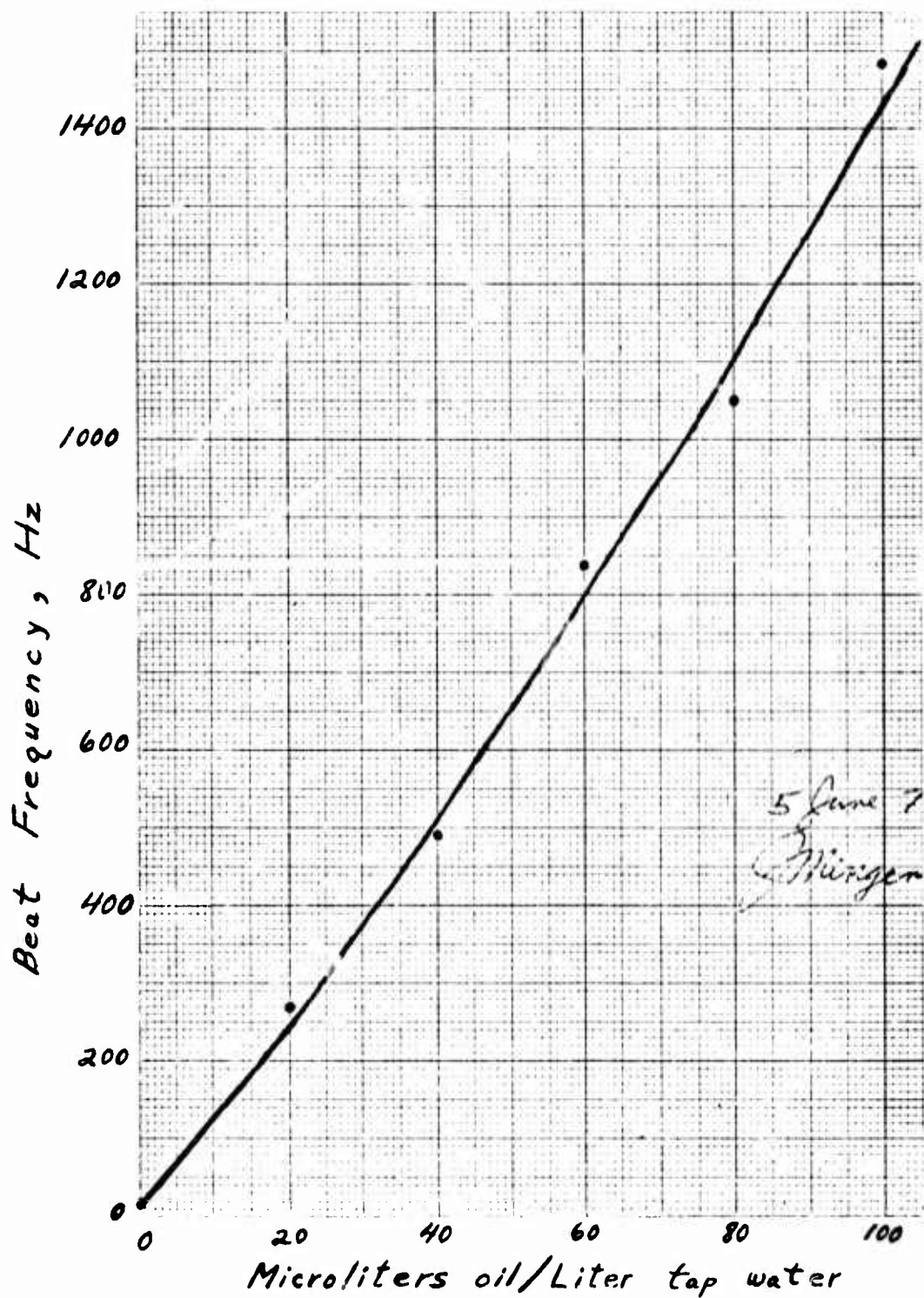


Fig. 4. Calibration curve for No. 2 diesel fuel/9250 lubricating oil mixture (5:1 by volume) in tap water. Seventy-milliliters water was shaken with 10-ml CH_2Cl_2 for 15 minutes. Beat frequencies were read after 3 minutes evaporation.

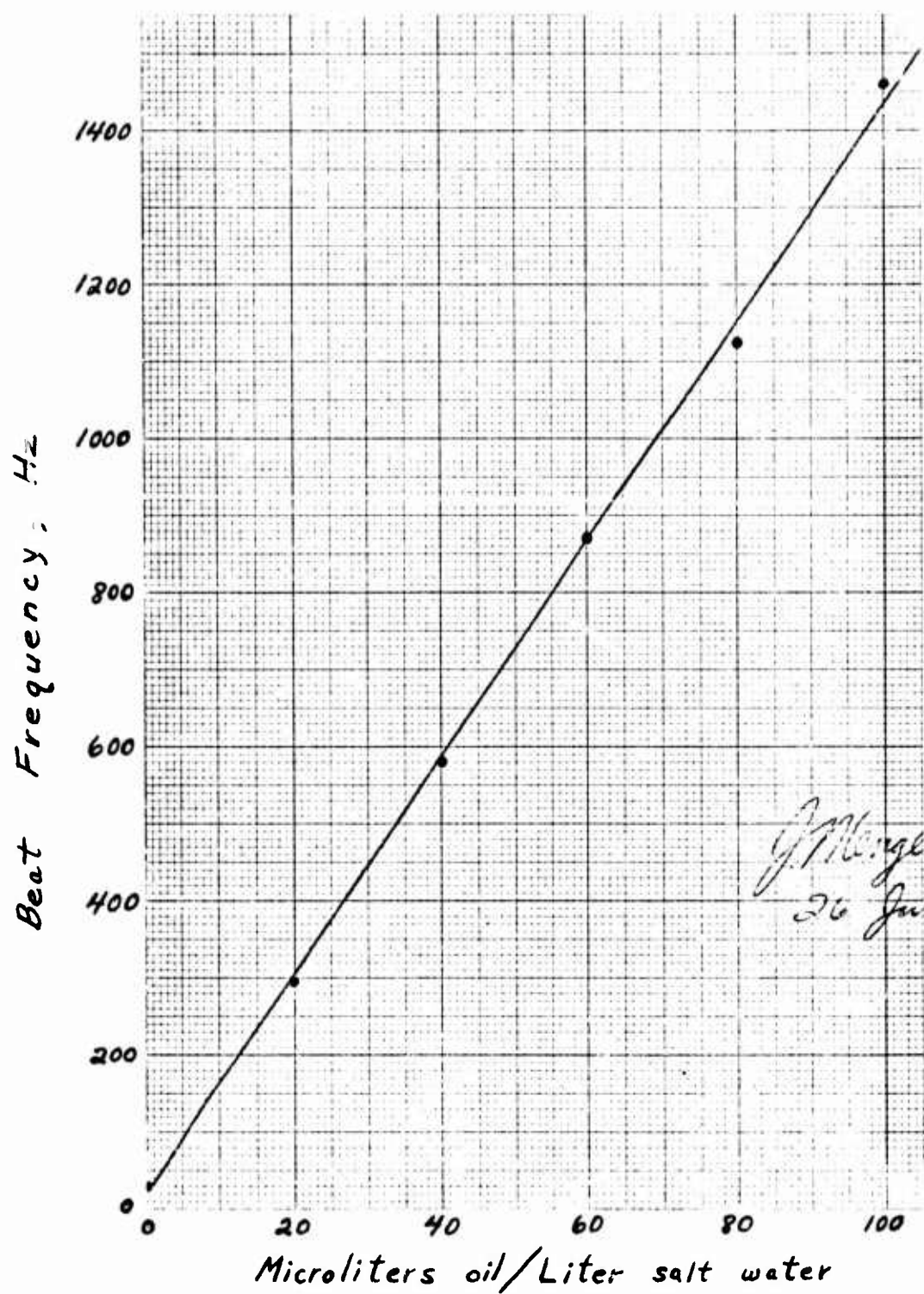


Fig. 5. Calibration curve for No. 2 diesel fuel/9250 lubricating oil mixture (5:1 by volume) in salt water. Seventy-milliliters water was shaken with 10-ml CH_2Cl_2 for 15 minutes. Beat frequencies were read after 3 minutes evaporation.

evaporated from the crystal within 3 minutes. The crystal microbalance is therefore not recommended for oils more volatile than No. 2 diesel fuel.

Several tests were made to see if the 2.00- μ l sample size was optimum. Response of the instrument was linear between 1.00 and 3.00 μ l, but samples of 0.50 μ l or less gave readings that were about 5 percent high when a 10- μ l syringe was used. Samples of more than 3 μ l tended to roll off the crystal. It was concluded that 2.00- μ l samples are about optimum but that any size between 1.00 and 2.50 μ l is satisfactory.

The residue after evaporation of the solvent was determined on the microbalance to see whether it was within the reagent grade specifications for CH_2Cl_2 . The average for five samples was 1.3 nanograms of residue per 2.00- μ l sample of solvent weighing 2.6 mg, or 0.5 ppm. The maximum residue for a single sample was 1.5 ppm. This value was well below the 20-ppm limit in the specification. In most cases the solvent residue is low enough to be neglected. The average beat frequency due to solvent residue was 3 Hz. It is evident that when the beat frequency due to oil is 150 Hz or more, the 3 Hz due to solvent residue is within the 2 percent random error and may be safely neglected. In any case, the residue of each solvent lot can be easily checked.

III. DISCUSSION

9. Concentration Ranges. The work discussed was designed to evaluate the microbalance in the 0- to 200-ppm range, and it was judged satisfactory for this purpose. No attempt was made to extend or modify the procedures for detection of smaller concentrations of oil. However, only minor changes in the procedures should make it possible to determine oil in the 0- to 10-ppm range. The ratio of water to extracting solvent could be increased to 50:1, or even to 100:1. Increasing the water to solvent ratio would also require a change of solvent because CH_2Cl_2 is slightly soluble in water. Carbon tetrachloride is quite insoluble in water and could be used, but the evaporation time may have to be increased because the vapor pressure of carbon tetrachloride is lower than that of CH_2Cl_2 .

10. Possible Interfering Substances. Since one of the potential applications of this instrument is analysis of oil in discharged bilge water, the presence of possible interfering substances must be considered. The most likely interfering substances are those materials extracted from water into CH_2Cl_2 but not considered to be oil. Some examples of these materials are ethylene glycol, plastics, sugar, and some types of paint and rubber. If a filter/coalescer-type separator is used to process the bilge water, the solid contaminants (paint chips, pieces of rubber, or plastic) should be removed, except in the somewhat unlikely event that these materials were somehow ground up into particles small enough to pass through the filter. The interference due to materials soluble

in both water and CH_2Cl_2 (sugar, ethylene glycol) would depend on the water to solvent ratio used in the procedure and on the distribution coefficient of the contaminant. Other less common contaminants that may cause interference are insecticides and waxes. Although these materials are not considered oil, they are often formulated with a petroleum base.

IV. CONCLUSIONS

11. Conclusions. It is concluded that:

- a. The sensitivity of the microbalance is about 4.3×10^{-10} g/Hz.
- b. The standard deviation of repeated readings of the same sample is about 2 percent of the mean.
- c. Calibration curves were constructed for Navy Distillate and No. 2 diesel fuel in tap water and for No. 2 diesel fuel/9250 lubricating oil (5:1 by volume) in tap water and salt water.