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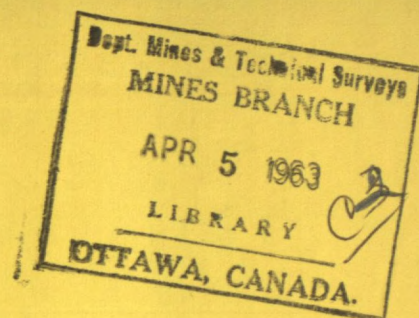
COMPETITIVE ADSORPTION OF C14-LABELLED OLEIC ACID BY QUARTZ AND HEMATITE IN FLOTATION PROCESSES

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by

C.M. Lapointe[*]

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SYNOPSIS

The adsorption of C^{14}-labelled oleic acid on quartz and

hematite has been studied in benzene for surface area measurements,

and in water for flotation purposes. Although the results on surface

areas for hematite agree with the expected values, those for quartz are

but a fraction of the values of a monolayer.

Contact and flotation tests in aqueous emulsions of oleic acid

showed a definite effect of even a small amount of quartz on the adsorption

of oleic acid by hematite, at near-neutral pH.

Improved techniques of radiometric measurements are described

for solutions, emulsions and films of oleic acid adsorbed on solids. A

new method for extracting the oleic acid from water with the liquid scintillator

and measuring its activity in a two-phase liquid system is described.

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COMPÉTITION ENTRE LE QUARTZ ET L'HÉMATITE DANS L'ADSORPTION DE L'ACIDE OLÉIQUE MARQUÉ AU CARBONE-14 AU COURS DE LA FLOTTATION

par

C.M. Lapointe[*]

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RÉSUMÉ

On a étudié l'adsorption par le quartz et l'hématite d'acide oléique marqué au carbone-14 en solution benzénique afin de mesurer l'aire des surfaces, et en solution aqueuse en vue d'obtenir des renseignements sur le mécanisme de la flottation de ces minéraux.

On a constaté que, alors que les aires mesurées sur l'hématite coïncidaient bien avec les valeurs prévues, les résultats obtenus avec le quartz ne correspondaient qu'à une fraction de la couche monomoléculaire d'acide oléique.

L'agitation et la flottation de mélanges de quartz et d'hématite en suspensions aqueuses d'acide oléique ont révélé une influence bien définie du quartz, même en faible proportion, sur la quantité d'acide oléique adsorbée par l'hématite à un pH voisin de 7.

On décrit des techniques améliorées pour la mesure radio-métrique de solutions, d'émulsions et de films d'acide oléique adsorbés sur les poudres. On a mis au point une nouvelle méthode qui permet l'extraction de l'acide de sa solution aqueuse par le scintillateur liquide et la mesure de son activité directement dans le système toluène-eau, à la température de la pièce, ou dans un système toluène-éthanol-eau en appareil réfrigéré.

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INTRODUCTION

Although the literature describing the techniques and patented methods of flotation for siliceous ores is extensive(1) and the comportment of pure hematite(2), magnetite(3) and quartz(4) towards various flotation agents has been thoroughly studied, there exists little information on the relative amounts of collectors adsorbed on the components of a mixture of these three minerals when the concentration of the collector, the temperature, the pH of the medium, and the nature and amount of depressant are varied systematically.

As a preliminary step to a more elaborate investigation of this problem, it was thought that the study of a simple system consisting of quartz, hematite and/or magnetite, and oleic acid in water in well-defined conditions might lead to the development of techniques and instrumentation suitable for tackling more complicated problems.

This report describes the equipment assembled in the Mineral Sciences Division laboratories for contact and flotation tests, for surface area measurements, for separation of the flotation products, and for the radiometric determination of the oleic acid content of liquid and solid

phases. It also includes some preliminary results on the partition of oleic acid between the quartz and the iron minerals in an aqueous medium during contaction and flotation.

For the convenience of the reader, the description of the equipment and procedures used for the measurement of the radioactive oleic acid has been separated from the text and appears as an Appendix following the list of references.

PREPARATION OF MATERIAL

Pure specular hematite was prepared from hand-cobbed high-grade iron ore, crushed to -65 mesh, and tabled in order to remove the quartz. The material was then leached with water to remove soluble impurities, dried, and further purified on a laboratory magnetic separator, which eliminated almost all the magnetite. The -65+100 mesh fraction was further cleaned with benzene in an ultra-sonic cleaner, in order to remove traces of grease and other organic matter, dried at 105°C, and stored for tests.

Pure magnetite was prepared from a magnetic-separator concentrate produced in the Division's laboratories. It was pulverized

to -65 mesh, tabled, and leached with water. The -65+100 mesh fraction

was cleaned with benzene like the hematite, dried, and retained.

Determinations of ferrous and ferric iron on the hematite and the magnetite

gave values slightly lower than theoretical, and the acid-insoluble residue

showed about 0.5% silica and silicates.

The quartz used was the -65+100 fraction of a purified sample

obtained from the Extraction Metallurgy Division. It was further cleaned

by leaching and by passing through a Frantz Isodynamic Separator,

degreased in the usual way, dried, and stored.

DETERMINATION OF SURFACE AREAS

A knowledge of the surface areas of the materials to be floated,

although not indispensable, is nevertheless of great help in the study

of flotation processes. Measurements on +100 mesh materials by nitrogen

adsorption (B.E.T. method) have proved difficult and not too reliable,

and the tendency now is to use, whenever possible, sorption methods

with radioactive tracers in solution(5). C^{14}-labelled oleic and stearic

acids in solution in benzene are the most widely used organic sorbates.

Powdered metals and most stable oxides as well as most non-hydrophilic

salts adsorb a long-chain organic acid from its solution in a non-polar

solvent. The sorption may be partly physical, partly chemical, and

the amount of acid adsorbed on the solid is proportional to the final

concentration of the solution up to the point where a monolayer of acid

is present on the solids. The values thus obtained for surface areas

agree fairly well with those obtained by nitrogen adsorption in the range

where this method is reliable.

Hematite and magnetite belong to the group of stable oxides for

which the adsorption seems to be a purely physical phenomenon, because

it is reversible. Silica, although highly stable, has a complex surface

structure which varies with the history of the sample and the treatment

to which it has been subjected. The fact that silica seems to have more

affinity for water and short-chain aliphatic alcohols than for long-chain

acids further complicates the measurement of its surface area by

sorption. Samples vacuum-dried at 100°C for some hours and treated with dry

benzene solutions of stearic acid in closed containers have shown surface

areas five times smaller than those obtained by nitrogen adsorption,

although the amounts of stearic acid in solution were equivalent to

several monolayers(6).

As only approximate values were required for this study, some

five-gram samples of material were dried at 160°C for four hours at

atmospheric pressure and cooled in a desiccator over silica gel.

Five ml of C^{14}-labelled oleic acid solution in benzene was added, the

concentrations being varied so as to supply as much as forty times the

amount of acid required for a monolayer on the expected surface areas.

The sample vials were clipped on to a 12-inch disk, which could rotate at

2 rpm, and the mixtures allowed to contact for two hours. 500 λ aliquots,

taken before and after contaction, were measured in a liquid scintillator, and the isotherms were computed. Table 1 shows the results obtained with quartz and hematite; the corresponding isotherms appear in Figure 1.

TABLE 1

Surface Area Measurements of Quartz and Hematite, -65+100 Mesh

Oleic Acid Concentration (μg/ml)	Surface Areas (cm^2/g)	
	Quartz	Hematite
60	56.7	135
120	73.7	182
180	77.8	192
240	80.8	204
300	82.0	198
360	80.0	200
480	84.0	202

As the surface area of a -65+100 mesh sample of quartz should be between 250 and 350 cm^2/g (7), it appears that water, either incompletely removed or dissolved in the benzene solution, interfered with the adsorption of the oleic acid and prevented the completion of a monolayer, even at concentrations such that the ratio of the final to the initial concentration was 0.95.

The result obtained for hematite, 200 cm^2/g, is in reasonable agreement with an expected surface area of about 225 cm^2/g, a value
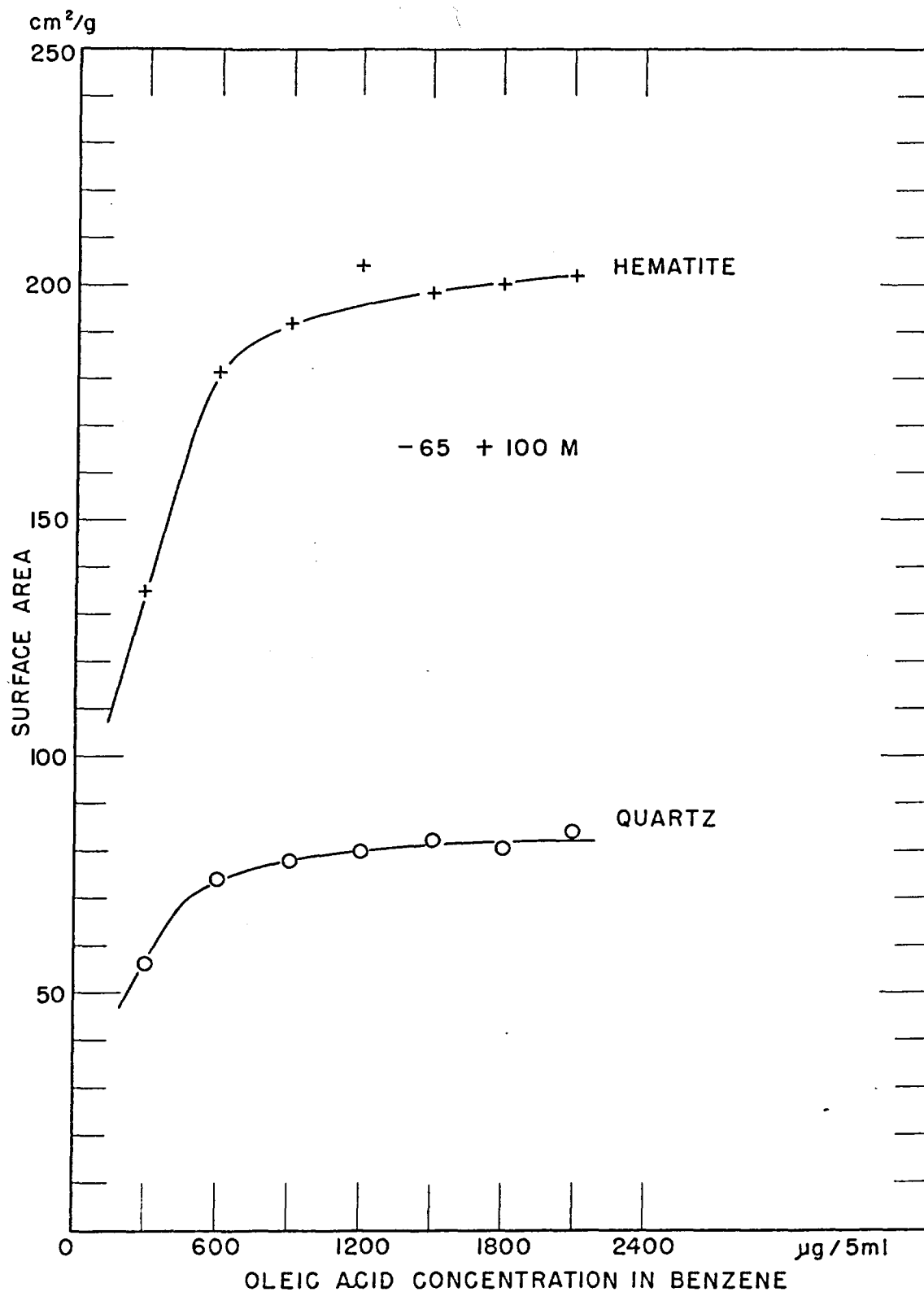
FIGURE I. SURFACE AREAS OF QUARTZ AND HEMATITE.

somewhat lower than that for quartz of the same size range, because of smoother cleavage surfaces.

In order to dry a batch of samples in a vacuum at a controlled temperature and to introduce the oleic acid solutions without admittance of water vapour, a vacuum distillation receiver has been modified as shown in Figure 2. A heating coil is installed in a porcelain insulator, at the bottom of the receiver, under a copper plate on which eight sample vials can be placed. The temperature is controlled with a Variac transformer, and can be raised to 300°C. The receiver is connected to a high-vacuum system through flexible couplings and provision has been made for the introduction of pure gases or air at a controlled moisture over the samples. The vials can be rotated under the tip of a specially designed burette for the admission of the oleic acid solution. .

The results on test runs seem promising, but actual area determinations have had to be postponed until perfectly dry oleic acid solutions have been prepared. It is also quite possible that the presence on the quartz surface of hydroxyl groups, which are not readily condensed at low temperatures, may prevent the formation of an organic monolayer on a perfectly dry surface (8, 9).
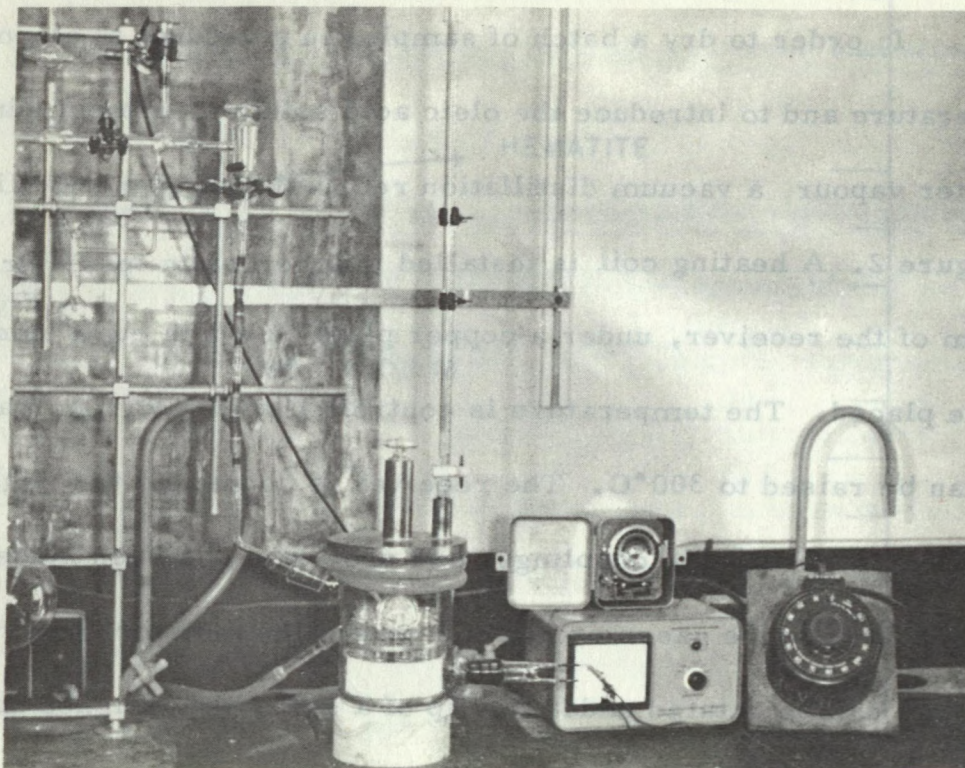
Figure 2.   Apparatus for drying samples in vacuum at controlled temperatures.

FLOTATION TESTS ON QUARTZ AND HEMATITE

All flotation tests were run on 20 g samples in cylindrical glass cells provided with a fritted-glass bottom, thus allowing admission of air for floating, or application of vacuum for the collection of the non-floated fraction (Figure 3). The floated fraction was skimmed into a funnel having a fritted-glass bottom, and a moderate vacuum was maintained there, for washing and drying of the material.

The preparation of a solution or of a homogeneous emulsion of oleic acid is always a problem, because of the low solubility of the acid in water. Some workers have used ethyl alcohol as a mutual solvent, but, as it was felt here that such a practice might alter the frothing conditions, a measured amount of oleic acid in benzene was pipetted onto the water in a beaker, and the solvent was allowed to evaporate in a draft at room temperature. Radiometric checks on the oleic acid content of the water showed that very little, if any, oleic acid was lost in the process.

In spite of its slight solubility in water, oleic acid ionizes over a wide range of pH (10). Table 2 shows the pH measured in 10 ml of water, over which varying amounts of an oleic acid solution in benzene have been evaporated. In the presence of an excess of oleic acid floating on the surface, the pH of the solution was 3.7, and this value did not change after ultrasonic agitation had emulsified most of the excess acid, resulting in an opalescent, fairly stable suspension.

STIRRER

FRITTED GLASS-M

3 BAFFLES

FRITTED GLASS-M

VACUUM

VACUUM OR PRESSURE

SCALE- CM

0   2   4   6   8
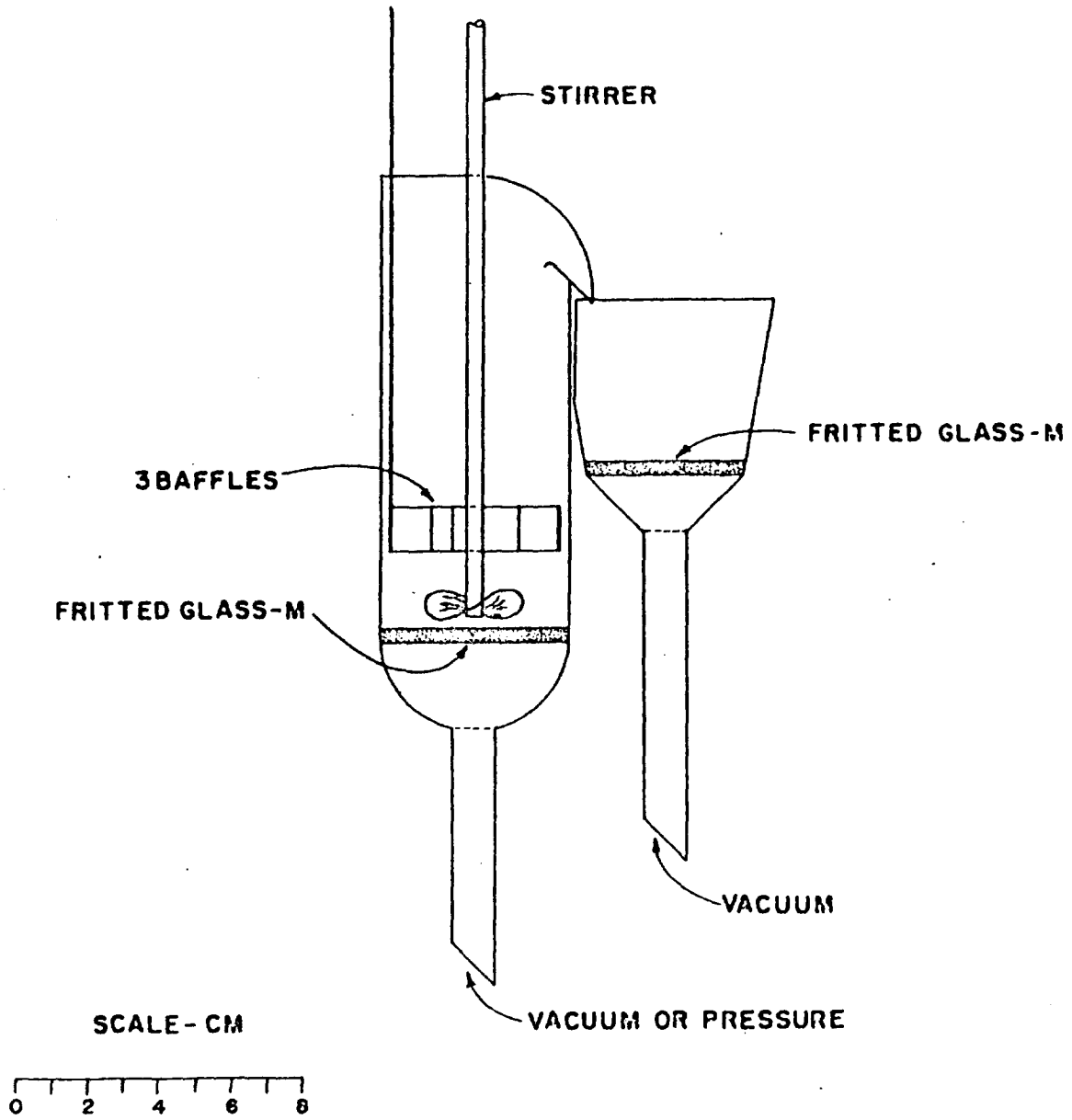
Figure 3.   Flotation cell.

TABLE 2

pH of Aqueous Oleic Acid Solutions

Oleic Acid in 10 ml H_2O (mg)	pH
0.6	5.75
1.2	5.35
1.8	5.25
2.4	5.15
3.0	5.05
6.0	4.60
9.0	4.40
12.0	4.30
15.0	4.20
Saturation	3.70

The first series of tests consisted in floating the separated minerals, in order to evaluate the fraction of the surface area to be coated with oleic acid for optimum recovery. This fraction, in the case of hematite, has already been reported(1) as between 7 and 15 per cent. The results obtained here confirmed these figures.

Using oleic acid in concentrations ranging from 0.02 to 0.2 lb/ton, it was found that from 50 to 96% of the hematite was readily floated. Increasing the amount of oleic acid beyond 0.2 lb/ton did not improve the recovery. An examination of the non-floated fraction at

0.2 lb/ton showed that most of the hematite grains contained varying

amounts of what appeared to be silica or silicates.

In the case of quartz, it was found that a sample that had been

soaked in water before addition of oleic acid had little tendency to float,

while a bone-dry sample poured into water already containing the acid

could be floated with a recovery of about 30 per cent. Examination of the

float and non-float fractions did not reveal any apparent difference, but

radiometric determinations showed that the floated fraction contained

about four times as much oleic acid as the other.

As the tests on magnetite produced results similar to those

obtained with hematite, the next series of tests consisted in floating

various mixtures of quartz and hematite at different oleic acid concentrations.

In the flotation of separated minerals, the estimation of the amount of

oleic acid adsorbed on the solids is easily done by measuring the activities

of aliquots of the solution before and after flotation, allowing for any

dilution due to the addition of water. But with mixtures one must be

able to separate the minerals without disturbing the oleic acid coating

on the grains and to determine the amount of acid adsorbed on each

fraction.

With quartz and hematite, separation on a Frantz Isodynamic

Separator has proved rapid and efficient. The flotation products are

washed twice with a minimum amount of water, dried at 90°C, and separated.

Some mixtures, especially those which had been floated at high oleic

concentrations, were difficult to separate because of a piling-up of the quartz in the vibrating trough. As this effect was due to electrostatic charging of the particles by friction, a radioactive strip of "Ionotron"[*] was mounted on the face of the upper pole of the separator; the intense ionization produced discharged the grains and restored free-flowing conditions. Results of typical runs are shown in Table 3.

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[*] "Ionotron" is a thin strip of nickel impregnated with a deposit of Radium D and E. The alpha particles emitted ionize the surrounding atmosphere. It is available from Atomic Energy of Canada Ltd., Ottawa.

TABLE 3

Flotation of Quartz and Hematite, -65+100 Mesh;
Distribution of Oleic Acid on the Separated Minerals (20-gram Samples)

Oleic Acid (lb/ton)		Quartz		Hematite	
		Float	Sink	Float	Sink
0.02	Distribution, %	4.0	96.0	48.0	52.0
	Oleic acid, arb. units	1200	120	2030	400
	" " , dist. %	32.0	3.2	54.0	10.8
0.08	Distribution, %	7.0	93.0	82.0	18.0
	Oleic acid, arb. units	2490	190	3150	1150
	" " , dist. %	35.7	2.7	45.1	16.5
0.20	Distribution, %	18.0	82.0	96.0	4.0
	Oleic acid, arb. units	3810	700	5960	3010
	" " , dist. %	28.2	5.2	44.2	22.4

These results indicate that the floated quartz fraction contains much more oleic acid than the non-floated one, a fact which indicates that the quartz was actually floated, and not merely brought to the surface by mechanical entrainment with the hematite. A cleaner float did not materially improve the separation. Microscopic examination of the floated quartz showed a fine reddish coating, no doubt due to the attrition of hematite. This effect was more pronounced in the contact runs.

Contact Tests

Measurements of oleic acid content in flotation tests are at best approximate, because of inevitable losses due to frothing, filtering and washing. For studying the partition of oleic acid between the minerals, it was thought more convenient to agitate the mixtures in the aqueous medium in small vials, as was done in the surface area determinations.

Test A - The Initial Concentration of Oleic Acid is Constant, the Proportions of Quartz and Hematite Vary

The oleic acid was introduced into the water by evaporation of a benzene solution over it, as in the flotation tests, and the mixtures of quartz and hematite in water were contacted for periods of time ranging from one to five hours. Agitation was as gentle as possible, in order to minimize the attrition of the hematite by the quartz. Table 4 and Figure 4 show the distribution of the oleic acid on the separated minerals. In this test, the proportions of quartz and hematite were varied, while the quantity of oleic acid, 350 μg, corresponding to one monolayer on the solids, was the same for each test.

While no study was made of the effect of the duration of agitation on the results, it was noticed that the total uptake of oleic acid by quartz increased with the agitation time; as mentioned earlier, this seemed to be caused by an increase in the amount of quartz becoming coated with hematite. No reason can be advanced as to why a portion of the quartz, as evidenced by the flotation tests, becomes coated with hematite while the remaining fraction does not.

TABLE 4

Distribution of Oleic Acid on Quartz and Hematite after
Agitation in an Aqueous Solution (6-gram Samples)

Percentage of Quartz in Mixtures	Specific Activities*		Oleic Acid Adsorbed*		
	Quartz	Hematite	Quartz	Hematite	Total
0	-	6080	-	36480	36480
16.6	2400	8006	2400	40030	42430
33.3	1380	10035	2760	40140	42900
50.0	1147	12550	3400	37650	41050
66.6	960	14820	3840	29640	33480
83.4	1450	22340	7250	22340	29590
100.0	2360	-	14160	-	14160

*The amounts of oleic acid are expressed in arbitrary units.

An analysis of the results shown in Table 4 reveals that, as
long as hematite constitutes at least 30 per cent of the mixture, it has a
definite influence on the amount of oleic acid adsorbed by the quartz; the
specific activity of the quartz shows a slight decrease with increasing
percentage of quartz, and the total amount of acid adsorbed on the quartz
increases but moderately, until the percentage of hematite is so small that
the quartz behaves as if it were the sole constituent of the solid phase. Then,
its oleic acid uptake becomes significant. The case of hematite is different:
the oleic acid adsorbed on this mineral when it constitutes from 50 to 100 per
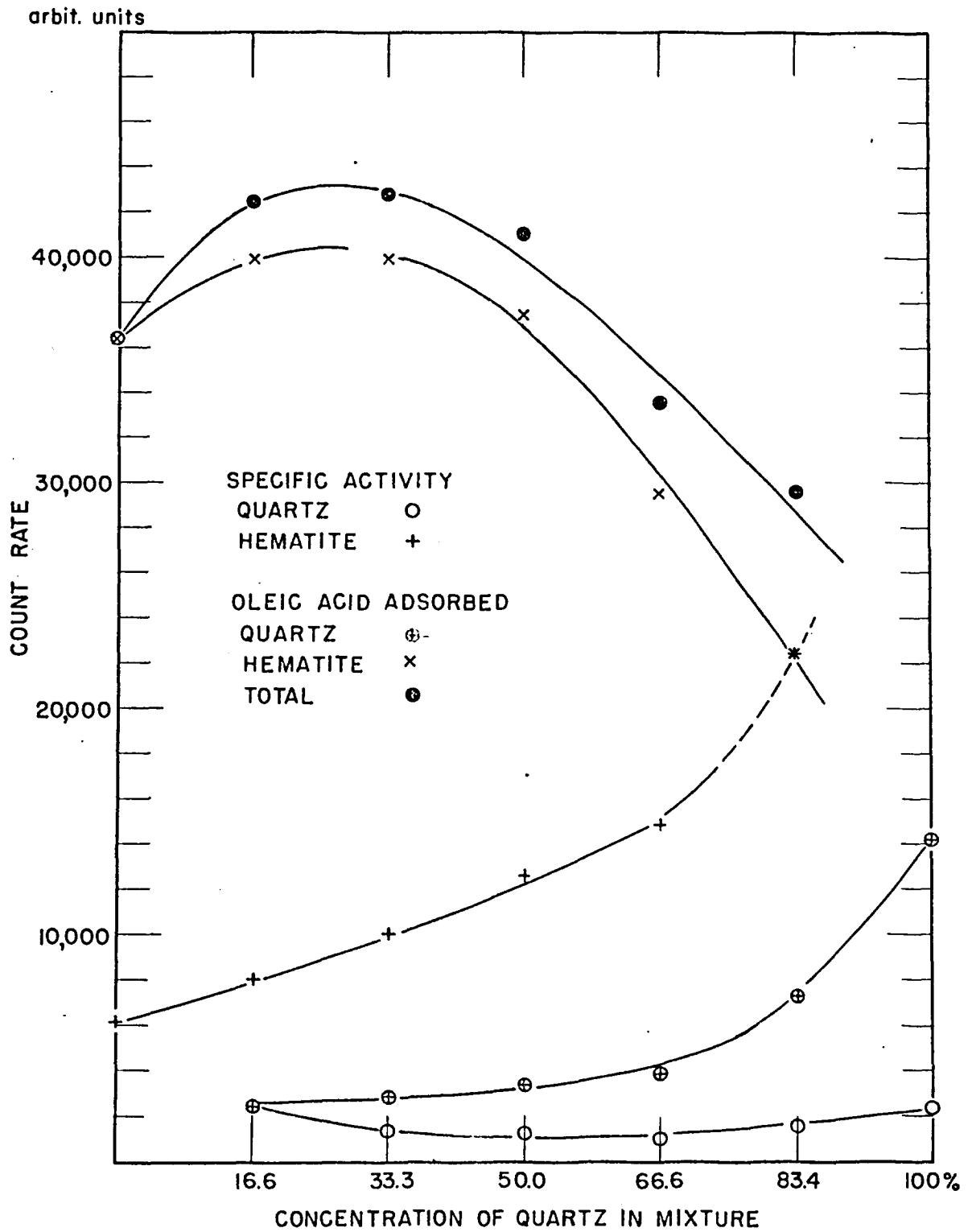cent of the solids is almost constant, the specific adsorption increasing

arbit. units

FIGURE 4. DISTRIBUTION OF OLEIC ACID ON QUARTZ AND HEMATITE
AFTER AGITATION IN AN AQUEOUS SOLUTION.

steadily as the amount of hematite present decreases. When this amount

becomes less than 50 per cent, there is a sharp drop in the total adsorption,

indicating a more extensive coverage of the grain surfaces and, possibly,

a more difficult replacement of the adsorbed water molecules by oleic acid.

It was noted that the final concentration of oleic acid remained

high, even at high hematite content; the largest amount adsorbed was only

25 per cent of that initially present, and the highest specific activity

obtained for hematite represented only 12 per cent of a monolayer.

Test B - The Proportions of Quartz and Hematite are Constant, the Initial Concentrations of Oleic Acid Vary

In this test, samples of quartz, hematite, and mixtures of both in

equal proportions were contacted in aqueous solutions where the oleic acid

content varied from 36 to 180 µg per gram of solids. The operating conditions

were the same as in Test A. In order to maintain constant the initial acid

concentration as well as the amount available per gram of solids, 5 ml of

solution was used for the 5-gram samples of quartz and hematite, and

10 ml for the 10-gram samples of mixed quartz and hematite. Table 5 and

Figure 5 show the results obtained in this test. For all oleic acid concentrations

except the lowest one, the quantity of acid available was greater than that

required for one monolayer (23 µg oleic acid represents a coverage of

100 cm^2).

TABLE 5

Adsorption of Oleic Acid from an Aqueous Solution by Quartz and Hematite and by a Mixture of the Two Minerals

Volume of Solution [*] Conc. Oleic Acid, (μg/ml)	5 ml 5 g Quartz	5 ml 5 g Hematite	Sum	10 ml Mixture 5 g Quartz + 5 g Hematite		Sum
36	110	280	390	130	200	330
72	220	625	845	280	530	810
108	350	855	1205	350	790	1140
144	455	1030	1485	390	1380	1770
180	555	1210	1765	480	2300	2780

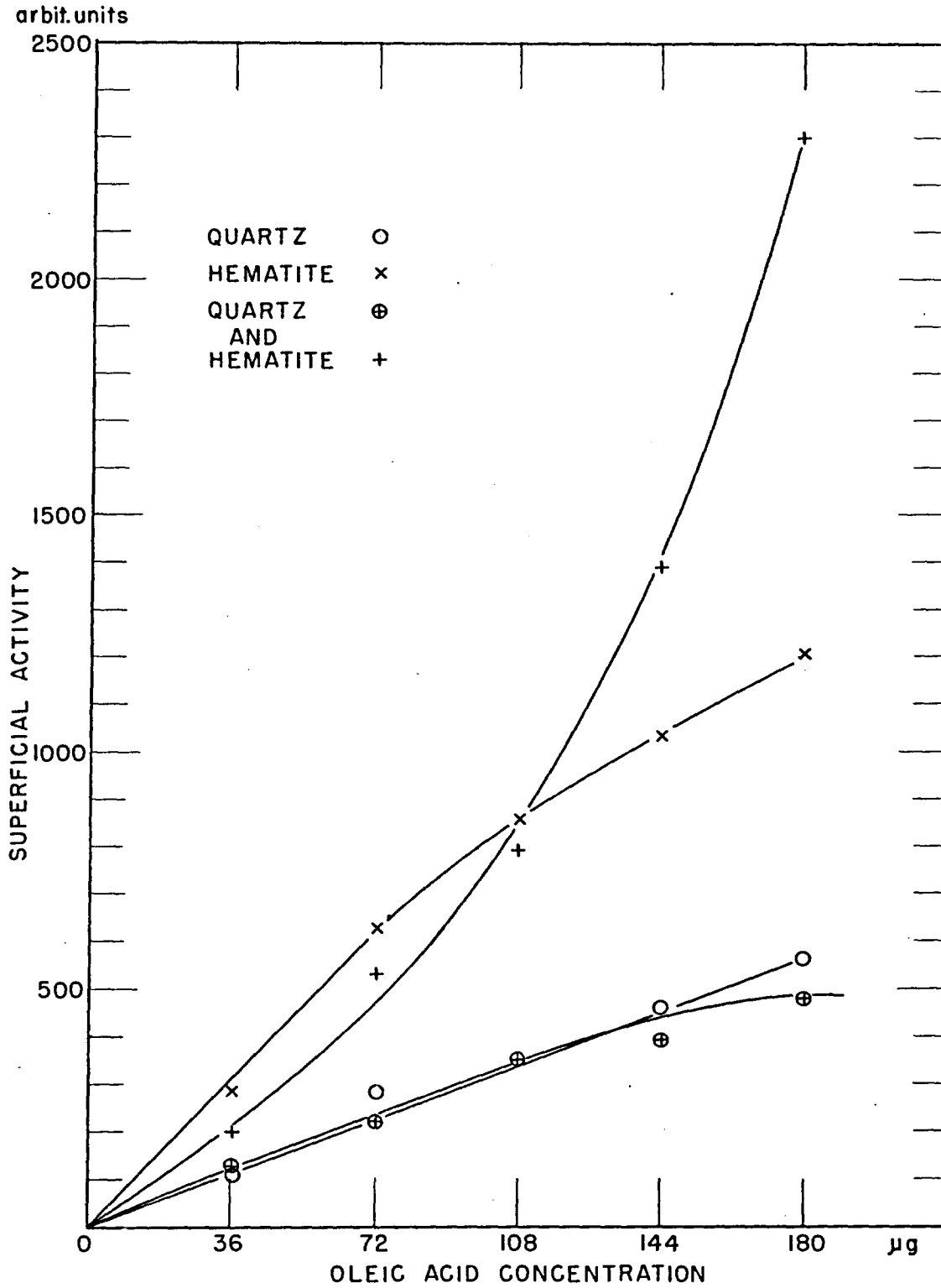[*] The amounts of oleic acid are expressed in arbitrary units.

FIGURE 5. ADSORPTION OF OLEIC ACID FROM AQUEOUS SOLUTIONS OF
VARYING CONCENTRATIONS BY QUARTZ, HEMATITE, AND
MIXTURES OF BOTH MINERALS.

The values obtained for adsorption on the minerals contacted separately indicate a slight departure from proportionality with respect to the initial concentrations, and they resemble those obtained at low acid concentrations in organic solvents. The effect is more evident in the case of hematite, for which the isotherm is decidedly concave.

On the other hand, the adsorptions measured on the minerals contacted together show that the quartz is a poor competitor with hematite: at the highest concentrations, it adsorbs less than when it is alone, although the amount of oleic acid available has been doubled. The hematite adsorbs quantities of oleic acid proportional to the amounts available in the solution when these amounts are large compared to what is adsorbed by the quartz, the only limitation being that the final concentration of the solution reaches some kind of potential equilibrium at the liquid-solid interface.

CONCLUSIONS AND OUTLINE OF MORE DETAILED WORK

The results presented in this report are preliminary and constitute only indications in the choice of problems and techniques. It seems evident that hematite and quartz belong to two different types of organic acid sorbants, at least at pH values determined only by the dissociation of the organic acid.

Work now in progress in these laboratories, includes, besides improvements in the techniques of radiation measurement, studies of the following: dissociation of the oleic acid at various pH values; the degree of association

of non-dissociated acid molecules when subjected to ultrasonic agitation

(formation of micelles); the role of sodium silicate and of silica slimes

as depressants for quartz; and the tenacity of the organic acid-solid bond

by means of different types of washing, extraction, and fractional distillation.

ACKNOWLEDGEMENTS

REFERENCES

1. A.M. Gaudin. Flotation. McGraw-Hill Book Co., 2nd ed., New York
   (1957).

2. W.E. Keck, G.C. Eggleston and W.W. Lowry. A Study of the
   Flotative Properties of Hematite. AIME Techn. Bull.
   No. 763 (1937).

3. W.E. Keck and Paul Jasberg. A Study of the Flotative Properties
   of Magnetite. AIME Techn. Bull. No. 801 (1937).

4. A.M. Gaudin and C.S. Chang. Adsorption on Quartz from an Aqueous
   Solution of Barium and Laurate Ions. AIME Trans. 193,
   193-201 (1952).

5. C. Orr, Jr. and J.M. Dallavalle. Fine Particle Measurement. MacMillan Co., New York (1959).

6. M.C. Kordecki and M.B. Gandy. An Investigation on the Use of Radioactive Isotopes for Determining the Surface Area of Powdered Materials by Sorption Methods. Savannah River Operations Office Rep. SRO-55, Project No. A-446-3 (1961).

7. A.M. Gaudin and R.T. Hukki. Principles of Comminution-Size and Surface Distribution. AIME Tech. Publ. No. 1779, pp. 17 (1944).

8. G.J. Young. Interaction of Water Vapor with Silica Surfaces. J. Colloid Sci. 13, 67-85 (1958).

9. G.J. Young and T.P. Bursh. Immersion Calorimetry Studies of the Interaction of Water with Silica Surfaces. J. Colloid Sci. 15, 361-369 (1960).

10. P. Rabone. Flotation Plant Practice. 4th ed., Mining Publications Ltd., London (1957).

11. C.A. Ziegler, D.J. Chleck and J. Brinkerhoff. Radio-assay of Low Specific Activity Tritiated Water by Improved Scintillation Techniques; in Liquid Scintillation Counting. Pergamon Press, New York (1958).

12. L. Yaffe and K.M. Justus. Back-scattering of Electrons into G-M counters. J. Chem. Soc. Part 3, S-341 (1949).

13. E.R. Washburn, A.E. Beguin and O.L. Beckford. J. Am. Chem. Soc. 61, 1694 (1939).

APPENDIX

Radiometric Assay of Oleic Acid

Because of the low energies (maximum 150 keV, average 50 keV) of the beta particles emitted by carbon-14, the radiometric assay of material tagged with this isotope is delicate and the sensitivity of the measurements is low, especially when the tagged compound is adsorbed on a solid.

Most workers in the field of flotation have used either gravimetric or titrimetric methods for the determination of fatty acids. Lately, however, some have used thin-window or window-less counters to measure evaporated aliquots of solutions or adsorbed films on solids.

Oleic Acid in Solution

In this laboratory, whenever the radioactive oleic acid is in solution or emulsion, it is measured by liquid scintillation counting. Two liquid scintillation counting systems are in use. One, a Baird-Atomic Model 845 A, operates at room temperature and is used for most of the determinations. The other one, consisting of a specially designed scintillation head housed in a freezer and connected to a Nuclear-Chicago Model 132 B single-channel analyser, operates at -25°C and is used for very low activities, when the phototube thermal noise has to be reduced to a minimum.

In surface area determinations, the oleic acid is in solution in benzene, toluene or heptane, and any reasonable amount can be

introduced into the liquid scintillator without altering its sensitivity
to any great extent. The scintillating medium used here is a toluene
solution containing 4 g of 2,5-diphenyloxazole (PPO) and 50 mg of
1,4-di $\left[2-(5-\text{phenyloxazole})\right]$-benzene (POPOP) per litre[*]. In contact or
flotation tests, the oleic acid is either dissolved or emulsified in water,
and the toluene scintillator will dissolve only a very small amount of it.
It is necessary to use a mutual solvent, such as ethanol. A method
employing dioxane and naphthalene as a scintillator can also be used,
but its utilization is restricted to operation at room temperature. The
introduction of ethanol and water in an organic scintillator considerably
reduces the height of the light pulses produced by the radiation, and
thus impairs the efficiency of the detection. A further complication
arises from the fact that a maximum of two per cent of water will remain
in solution in a scintillator containing 33 per cent absolute ethanol at
-25°C (11). Some work has been done here on the feasibility of extracting
the oleic acid from the water with the scintillator, and of measuring the
activity directly on the organic-aqueous phases. The water layer, instead
of interfering with the phosphor, actually improves its efficiency by
removing most of the ethanol from the toluene.

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[*] Liquifluor, a comparable concentrated scintillator mixture, is
available from Pilot Chemicals Inc., Watertown, Mass.

A small amount of oleic acid in benzene was added to two 10-ml scintillator solutions, one with only toluene as the solvent, and the other with toluene containing 30 per cent absolute ethanol. Water was added, at first 100λ at a time, then 250λ at a time; the vials were vigorously agitated, then centrifuged for 10 minutes, and the activities were measured. Figure 6 illustrates the results obtained.

In the case of the pure toluene scintillator, the addition of 200λ of water produced quenching of the fluorescence resulting in a 4 per cent decrease in sensitivity. Further addition of water resulted in a slow decrease of the sensitivity, roughly proportional to the thickness of the water underlying the scintillator layer.

The system toluene-ethanol-water is more complicated. A look at the solubility and conjugation curves at 25°C (Figure 7) shows that the system will remain homogeneous until about 6 per cent of water has dissolved. Further addition of water will bring the system to the plait point P, where the densities of the toluene-alcohol and the water-alcohol mixtures are equal, and separation in two layers is impossible, even after repeated centrifugation. Addition of a small amount of water will increase the density of the alcohol-water phase, and the system readily separates into two layers. As the water removes more and more alcohol from the toluene phase, the sensitivity of the system increases until the two curves practically meet, after a total of 5.50 ml water has been added to each scintillator.
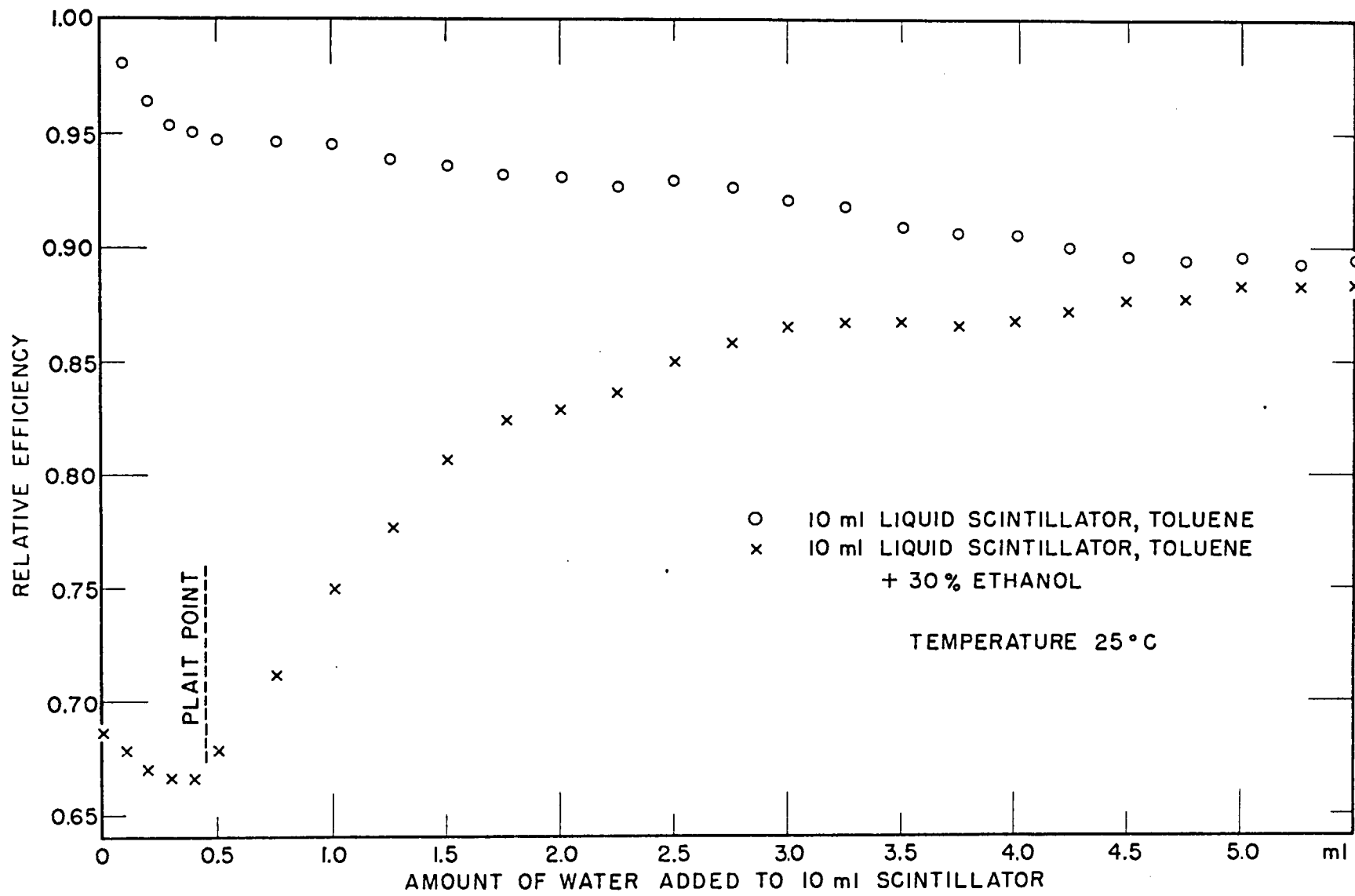
FIGURE 6. RELATIVE EFFICIENCIES OF TOLUENE AND TOLUENE-ALCOHOL
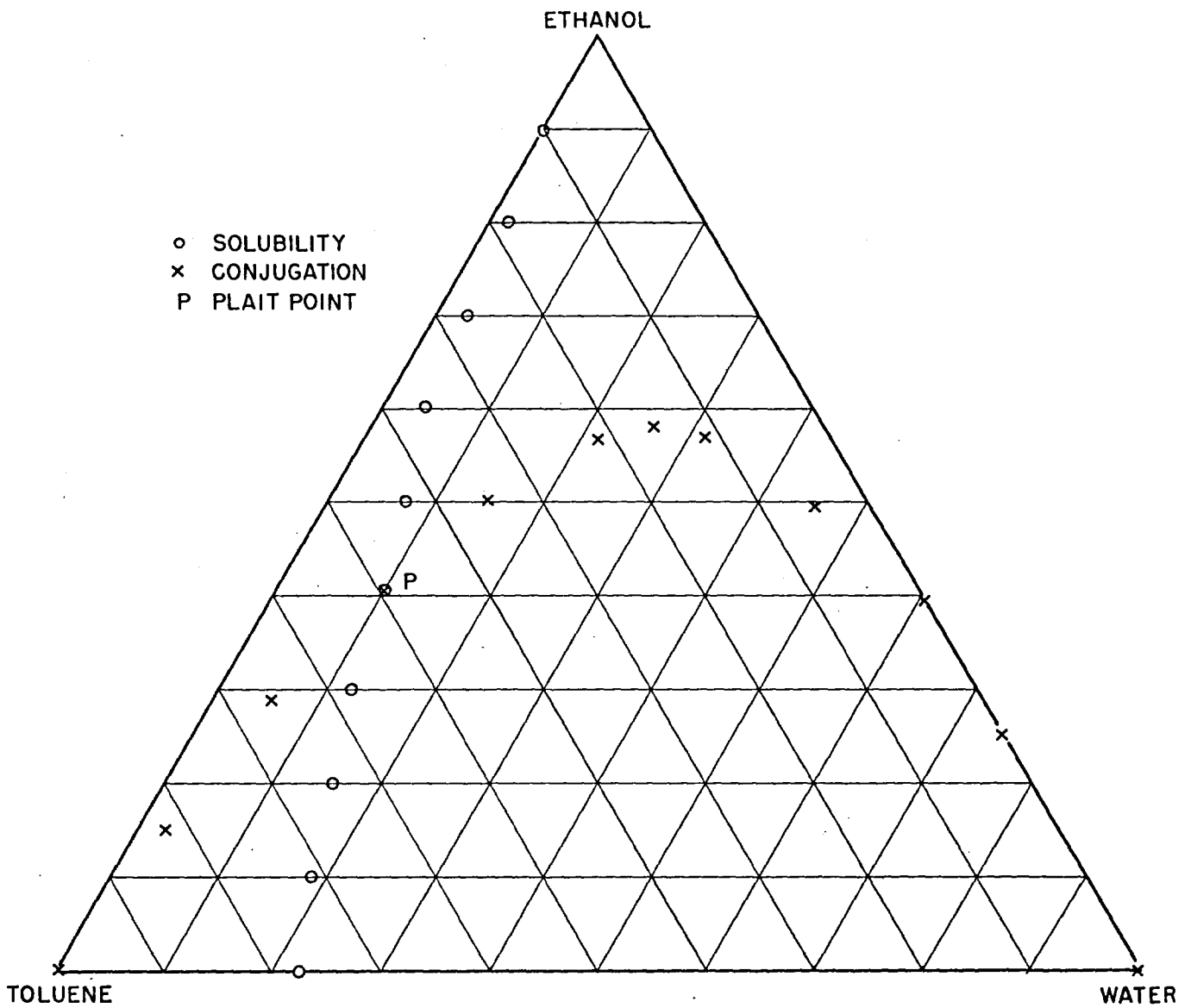SCINTILLATORS WITH ADDITION OF WATER.

FIGURE 7. SOLUBILITY AND CONJUGATION CURVES OF THE SYSTEM
ETHANOL – TOLUENE – WATER AT 25°C (AFTER REF. 13)

Because of the removal of most of the alcohol from the toluene phase, the scintillator layer in the toluene-alcohol-water system is located farther away from the face of the photomultiplier. Addition of 1.50 ml of water to the toluene-water system equalizes the geometry of the two systems, and the sensitivities agree within less than 1 per cent.

Although measurements were not performed at low temperatures, it was found that the toluene-alcohol-water system remained liquid and transparent at -35°C, even when containing 35 per cent water. For operation at room temperature, the toluene-alcohol system is more sensitive, especially for small amounts of water.

Oleic Acid Adsorbed on Solids
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The activity of adsorbed films of radioactive oleic acid is usually measured with very thin mica- or Mylar-window counters, or in windowless flow counters. As the range of the C^{14} beta radiation in silica and hematite is very short (maximum 20 mg/cm^2, average 12 mg/cm^2), only the oleic acid adsorbed on the surface of the mineral grains forming the top layer of the sample is actually measured. This results in poor sampling, and very low counting efficiency.

Fairly active samples have been counted under a Geiger counter with a mica window of thickness equal to 1.9 mg/cm^2, in a manual sample changer. Moderately active samples can be measured overnight in an

automatic sample changer and record printer. This unit (Figure 8) can handle 25 samples, and the counting cycle may be repeated until the desired statistical accuracy is obtained.

Samples of low activity are counted in a flow-counter operating in the proportional region. The 2π counter was obtained from the Chalk River laboratories of Atomic Energy of Canada Ltd. The quenching gas is a mixture of 10% methane and 90% argon, available commercially[*]. The pulses from the counter, operating at about 2000 volts, are fed directly to a Victoreen model S3HVD amplifier and scaler. Because of the geometry of the counter, the sample itself constitutes part of the cathode and must be a reasonably good conductor of electricity, in order to maintain constant the field between the electrodes. Hematite and magnetite are good conductors, and bare samples can be used. But the quartz powders, because of their high resistivity, accumulate positive ions at their surfaces, and the effective voltage between anode and cathode slowly decreases, with a resulting loss in counting efficiency. It is thus necessary to cover all non-conducting samples with a thin metallic diaphragm, in this case an aluminum foil of thickness $150 \mu g/cm^2$ rigidly mounted on an aluminum annulus.

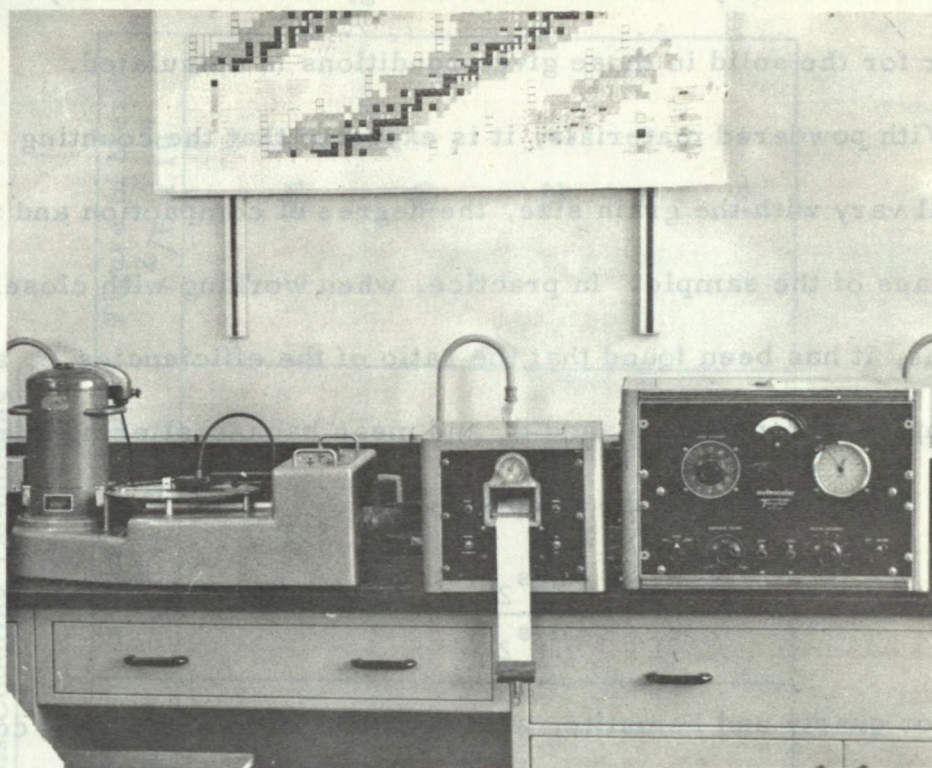[*] Matheson of Canada Ltd., Whitby, Ont.

Figure 8. Automatic counting system.

Correlation Between Activities Measured on Solids and Liquids

A direct determination of the efficiency of a counter for a

radioactive tracer adsorbed on a solid of thickness large compared to the

range of beta particles emitted by the tracer is possible only when the

amount adsorbed can be determined independently. This can be done

in the following way. The counting rate is measured on a given weight

of the sample in a well-defined geometry. Then, all the adsorbed tracer

is extracted from the solid in a micro-extraction apparatus of the Soxhlet

type, using a measured amount of a solvent compatible with the liquid

scintillator currently used. Finally, an aliquot of the extract is compared

with a standard solution by scintillation counting, and the efficiency

of the counter for the solid in those given conditions is calculated.

With powdered materials, it is expected that the counting

efficiency will vary with the grain size, the degree of compaction and the

superficial mass of the sample. In practice, when working with closely-

sized fractions, it has been found that the ratio of the efficiencies e_1 and

e_2 of two samples of densities d_1 and d_2 and mean back-scattering coefficients

s_1 and s_2 can be expressed by the simple relation

$$\frac{e_2}{e_1} = \frac{d_2 s_2}{d_1 s_2}$$

For quartz and hematite, with densities 2.65 and 5.24 g/cc,

and a ratio of back-scattering coefficients equal to 1.01, calculated from

the mean values of the atomic numbers of the molecules(12), $e_2/e_1 = 1.99$.

This value was confirmed to within one per cent by direct determination.

Operating Characteristics of Counting Equipment

The operating characteristics of the various types of counters

and counting methods have been summarized in Table 6. The values shown

here are not maximum for efficiencies, nor minimum for back-

grounds; the operating conditions, such as counter and phototube voltages,

volume of scintillator, and size of sample, have been chosen so as to reach

an optimum set of values representing a compromise between simplicity,

rapidity and accuracy of the measurements.

TABLE 6

Operating Characteristics for Various Counting Techniques

Technique	Efficiency (e) (counts/disintegration)	Background (B) (c.p.m.)	Figure of Merit $e^2/B \times 10^4$
Liquid scintillation counting			
10 ml pure scintillator	0.61	85	44
10 ml scintillator at 30% Ethanol, 0.1 ml aq. sample, one-liquid phase.	0.47	75	30
10 ml scintillator at 30% Ethanol, 2.0 ml aq. sample, two-liquid phase.	0.52	80	32
Proportional counting, thin source	0.34	54	21
Geiger counting, Anton tube, thin source	0.05	16	16

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