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DETERMINATION OF EVAPORATIVE LOSS FROM

CRUDE OIL BY GAS CHROMATOGRAPHY

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DETERMINATION OF EVAPORATIVE LOSS FROM

CRUDE OIL BY GAS CHROMATOGRAPHY

Hart, J.

J. Hart
Lakes Research Division
Canada Centre for Inland Waters
Burlington, Ontario, Canada

INTRODUCTION

A major factor affecting the physical and chemical nature of spilled oils is evaporation of volatile components. Crude oils of wide boiling ranges are most affected by evaporative losses that result in increased viscosity, lower spreading rates, and alteration of their ability to form water-in-oil emulsions or to disperse in the water. These evaporative losses can be substantial, (as much as 30-40% by weight depending on the oil's boiling range), and can occur in a very short time. A crude oil slick with a thickness of 100 microns could lose about 30% of its weight during the first hour of exposure under average conditions of light winds and mild weather. Thus crude oil was chosen as the principal oil in the development of a simple method to determine evaporative losses.

Methods that have been recommended for determining evaporative losses from aged oil samples are based primarily on measuring the concentrations of specific hydrocarbons (usually paraffins) in the fresh and aged crude oil. This is usually accomplished by a fractional distillation of the fresh crude oil followed by a G.C. analysis of the fractions for calibration purposes, along with G.C. analyses of the weathered and fresh crude oils.⁽¹⁾ If different crude oils are to be analyzed this type of determination can be very tedious. The method described in this report compares the complete chromatogram of a fresh sample of the oil to that of the weathered oil. This requires no identification of individual peaks on the chromatogram and, with a minimum amount of calibration, results in a rapid and simple analysis.

MATERIALS AND METHOD

Most of the experimental work was performed on a Western Canadian Crude Oil supplied by Shell Oil Company (Oakville, Ontario). Several pure hydrocarbons were used in addition for calibration purposes.

Earlier experiments indicated that evaporation from oil layers was independent of the presence of a water phase under the oil provided that the two layers were not agitated and were of the same temperature. All tests were carried out with the crude oil in preweighed beakers and Petri dishes exposed in a fume hood for evaporation. The containers were then reweighed to determine the actual losses. The samples were homogenized and a subsample was placed in a 5 ml vial for gas chromatographic analysis.

Chromatographic analyses were performed using a Hewlett Packard Model 5750 gas chromatograph equipped with dual columns and a flame ionization detector. The trace was recorded on a Sargent-Welch Model SRGC recorder and peak areas were given by a disc integrator. The G.C. conditions are summarized below:

Column Specifications:

Type: Stainless steel

Length: 4.0 feet

Diameter: 0.25 in. O.D. - thin wall

Packing: 5% SE-30 on 60/80 mesh

Chromosorb W (AW-DMCS)

Operating Conditions:

Injection Port - 280°C

Detector Port - 320°C

Initial Column

Temperature - 100°C

Final Column

Temperature - 280°C

Program Rate - 10°C per min. - Upper Limit

Hold for 5-10 mins.

Carrier Gas (He)- 24 ml./min.

Flame Detector: H₂ - 24 ml./min.

Air - 500 ml./min.

Recorder Speed - 0.5 in./min.

Preliminary trials indicated that reproducible sample size injections into the G.C. could best be accomplished using the full capacity of a 10 microlitre syringe. This was used as the sample size for all the G.C. injections.

The response factors of several pure hydrocarbons were measured and a log-log plot was prepared for a quick determination of the amounts of petroleum components that had passed through the chromatograph, as a function of peak area counts (Fig. 1). Although the response factors for aromatic compounds differ substantially from those of the aliphatic compounds, it was found that the petroleum

distillate Jet Fuel A-1 (which would elute completely from the column and contained both types) fell on the calibration curve. It was assumed that this response would hold true for the crude oil and aliphatic compounds were used for calibration.

Typical G.C. traces of fresh and aged crude oils are shown in Figure 2. The trace of the fresh oil sample shows considerable resolution for the low boiling components, the peaks being mainly paraffins over an aromatic base. The "tail ends" of the traces however, are more comparable for the two oil samples. It was soon recognized in these experiments from total peak area counts, that a considerable portion of the oil was not eluted from the chromatograph. For the fresh crude oil samples, this "residue" amounted to 36% (vol.) of the oil.

For the calculation of evaporation losses, the following quantities were determined:

- C_T = total peak area counts for the oil determined from the response curve. (For the same sample sizes, this value is the same for both fresh and aged oil)
- C_{LF} = peak area counts in the 0 - 18 min. section (100-280°C) of the chromatogram for the fresh oil sample.
- C_{LA} = the same for the aged oil sample.
- C_{HF} = $C_T - C_{LF}$ = the "peak area counts" of residues; i.e. components eluted and not eluted after the arbitrary cut-off point of 280°C for the fresh oil.

$C_{HA} = C_T - C_{LA}$ = the same for the aged oil sample.

The evaporation loss was then calculated from:

$$\% \text{ Evaporation Loss} = \frac{C_{LF} - \frac{C_{HF}}{C_{HA}} * C_{LA}}{C_T} * 100$$

The oil samples were all analyzed in triplicate. In cases where the aged oil was too viscous to be injected, a known fraction of benzene was used as a solvent. The integration of the peak area was initiated after the elution of the solvent peak, and no difficulties were encountered in the evaporative loss determination.

RESULTS

The results of 20 evaporation tests, using the Western Canadian Crude Oil, are summarized in Figure 3. The average deviation from the true evaporative loss values was $\pm 2.6\%$ with the maximum deviation being 5.1%. The repeatability of the method is illustrated in Table 1. These figures are within the generally accepted optimum performance range of a microlitre syringe in the hands of an experienced operator. The disk integrator was found satisfactory in the calculation of the peak areas and a comparison with an automatic printer yielded no significant difference.

RECOMMENDED PROCEDURE

With the gas chromatographic parameters set up as previously stated, inject 10 microlitre samples of pure hydrocarbons or volatile petroleum fractions. Plot a calibration curve of peak area as a function of sample size on a log. - log. graph.

Inject 10 microlitre quantities of the fresh crude oil and the weathered crude oil in triplicate maintaining the maximum column temperature for about five to ten minutes between runs to ensure return to baseline.

Determine the peak areas of the samples and using the calibration curve and the previously derived equation calculate the evaporative loss.

After about 50 analyses the injection port insert should be removed and the port cleaned. Baseline drifting and spiking are indications of the need to clean the port.

Backflushing of the columns will also decrease baseline drift and prolong column life.

CONCLUSIONS

The results of this experimental work show that gas chromatography can be used to give an accurate and rapid measure of the evaporative loss from a crude oil. With this method, once the initial calibration is completed, the evaporative loss of any type of crude oil could be determined by only obtaining a G.C. trace

of the weathered oil sample and that of the fresh oil sample in question.

Further work is planned on field sample preparation and a comparison of this method with a determination of evaporative loss by peak identification is underway.

REFERENCES

1. SCOTT, B. F., Dept. of the Environment, Ottawa, Ontario.
Personal communication (Dec. 1973).

TABLE 1

A

True Evaporative loss 35.7%

Trial: 1 38.8%

2 37.7%

3 35.5%

Avg. 37.3% ± 1.2 B

True Evaporative Loss 15.8%

Trial: 1 17.9%

2 19.5%

3 13.2%

Avg. 16.9% ± 1.1

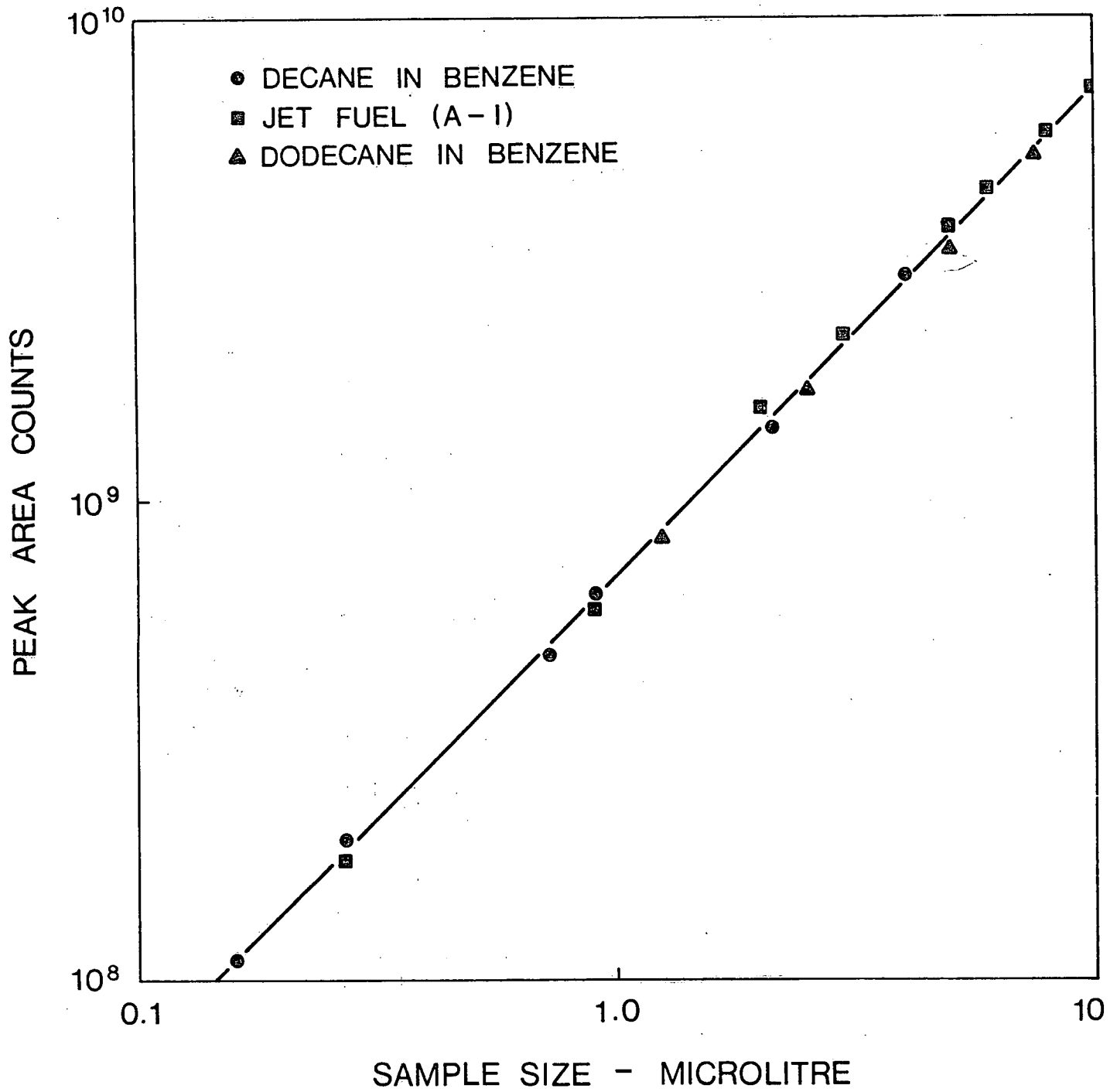


Figure 1 Calibration Curve

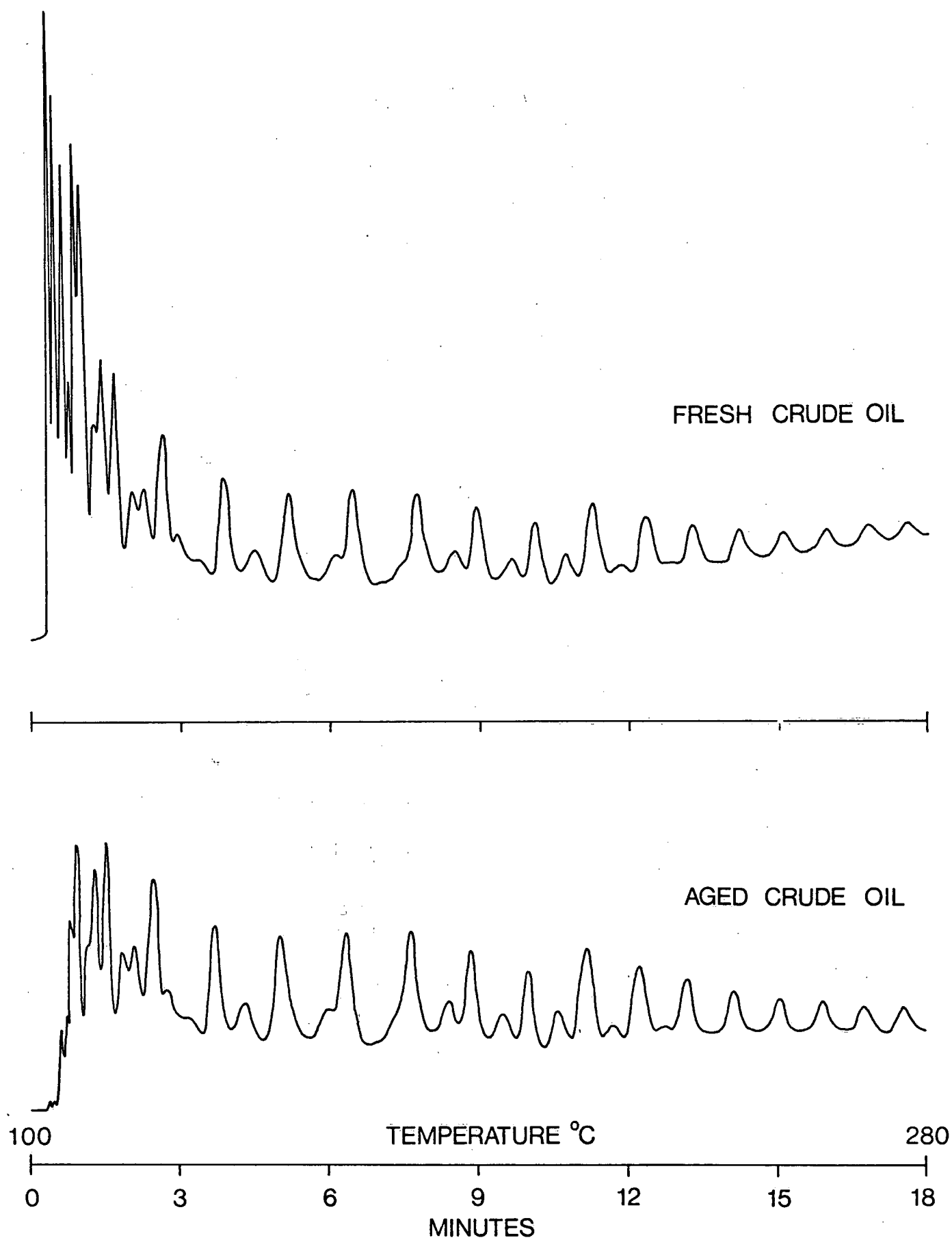


Figure 2 Typical fresh and aged crude oil chromatograms

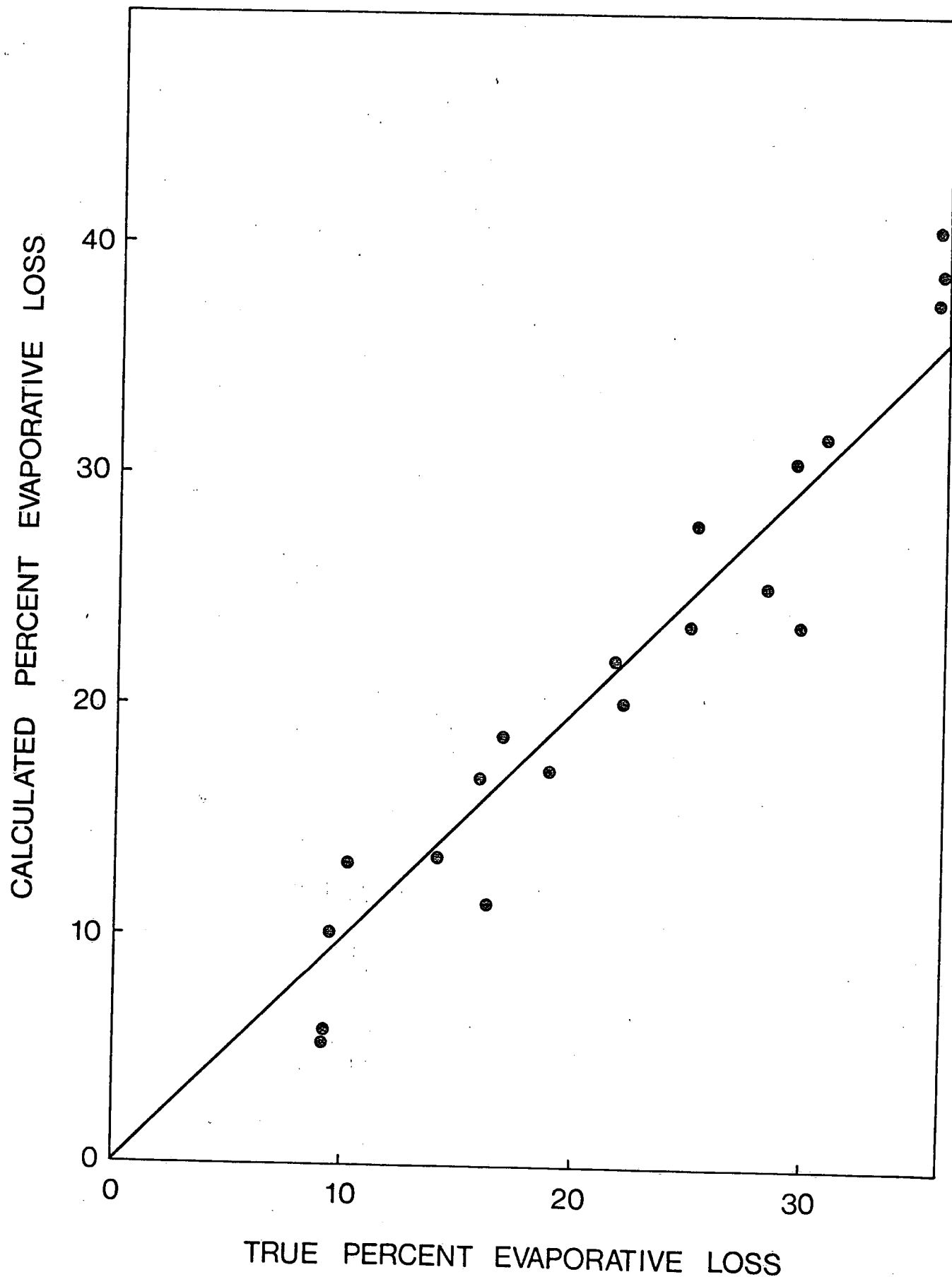


Figure 3 Calculated evaporative loss vs
True evaporative loss

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