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PRELIMINARY DRAFT

METHOD FOR ANALYSIS OF GASOLINE, DIESEL FUEL AND SIMILAR MATERIALS IN SOIL.

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SCOPE

This method is for the determination of gasoline, diesel fuel and similar hydrocarbon materials in soil samples obtained in investigating service station and other fuel storage sites. It is capable of detecting these fuels down to 10 ppm in soil. Repeatability and reproducibility have not been determined. Based on similar analyses using the same principles, repeatability is estimated to be +/- 20% or better.

Use of this method is restricted to persons experienced in quantitative gas chromatography using flame ionization detectors, integrators and the internal standard methodology.

PRINCIPLE

The soil sample is extracted with ~~carbon disulfide~~ ^{methylene chloride} CH_2Cl_2 to dissolve and concentrate hydrocarbons absorbed in the soil. An internal standard is added to the sample for quantitation. The carbon disulfide is recovered by displacement with water and centrifugation. The ~~carbon disulfide~~ extract is chromatographed and the area of the fuel peaks is compared to the internal standard to estimate the concentration in the soil.

REAGENTS AND EQUIPMENT

~~Carbon disulfide~~ ^{CH_2Cl_2} ~~Carbon disulfide~~, reagent grade. (See Note 1 for CAUTION)

- 40 mL VOA vials.
- Analytical balance.
- Pasteur pipettes.
- Volumetric pipettes - 1 and 5 mL.
- Volumetric flask - 50 or 100 mL.
- Distilled water.
- Ultrasonic bath.
- Centrifuge capable of accommodating VOA vials.
- Gas chromatograph with flame ionization detector and means of quantifying peaks.
- Injection syringe, 10 μ L.

Rep. as CS₂ with methyl blue

PROCEDURE

1. Pipette ~~10.00 mL heptane~~ ^{10.00 mL heptadecane (100 μ l heptadecane)} into a 100 ml volumetric flask and fill with ~~carbon disulfide~~ ^{CH_2Cl_2} . Mix. (Notes 2 and 3.)
2. Weigh 30 to 35 grams of the soil to be tested into a tared VOA vial and record the weight.
3. Pipette 5.00 mL of the ~~carbon disulfide~~ ^{CH_2Cl_2} - ~~heptane~~ ^{heptadecane} solution into the vial followed by 15 mL distilled ~~water~~ ^{WATE}.

Note 3. N-heptane is a component of gasoline and other hydrocarbon mixtures. It is added here as an internal standard in sufficient quantity so that its concentration in the final extract will be much higher than any heptane extracted from the soil.

Note 4. The water is added to the sample to facilitate mixing and to provide a liquid for displacing the ~~carbon disulfide~~ from the soil.

CH_2Cl_2

CALCULATIONS

Q3A2

hexadecane- CH_2Cl_2 standard:
1 ml hexadecane in
100 ml CH_2Cl_2 or
(1 μ l in 1 ml)

1. The carbon disulfide - heptane solution prepared in Step 1, PROCEDURE, contains 34.2 mg heptane in 5.00 mL. This is the internal standard weight, W_{IS} . The weight of soil, in grams, from Step 2 is the sample weight, W_{SAMP} . Estimate the area of the I.S. from the integration of Step 11. This is A_{IS} . Estimate the area of the hydrocarbon from the integration. This is A_{SAMP} . Use the Blank run from Step 13 to help estimate A_{SAMP} .

2. Make a preliminary calculation of the amount of hydrocarbon in the soil sample.

$$\frac{A_{SAMP} \times W_{IS}}{A_{IS} \times W_{SAMP}} \times 1000 = \text{ppm hydrocarbon (prelim)}$$

3. This preliminary calculation, coupled with qualitative identification of the hydrocarbon product, may suffice for decision making. Depending on the chromatographic conditions, the preliminary concentration will be approximately 50% - 90% of the true value. Careful standardation of the method may not be warranted in every case.

4. If more accurate calibration of the method is necessary, plot the ratio of A_{SAMP}/A_{IS} for each of the standards chromatographed in Step 14, PROCEDURE, vs. ppm hydrocarbon in the standards. Compare the A_{SAMP}/A_{IS} ratio of unknown samples to this calibration curve for quantitation.

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water. (Note 4).

4. Place the Teflon faced cap on the VOA vial and make sure the vial doesn't leak.
5. Shake vigorously for two minutes. Sonicate for 2 minutes in an ultrasonic bath.
6. Repeat step 5 twice.

7. Centrifuge the sample vial for 15 minutes at 2500 RPM. (40) (100)

8. Sample will now consist of three layers. The bottom layer is the soil. On top of that will be the ~~carbon disulfide~~ layer and on that, the water.

9. Remove the ~~carbon disulfide~~ layer with a Pasteur pipette and place in a small vial with a teflon lined cap. Refrigerate until analyzed. It is unnecessary to recover all the ~~carbon disulfide~~ added.

10. Chromatograph the ~~carbon disulfide~~ on a gas chromatograph with a flame ionization detector (FID). Table I gives some suggested chromatographic conditions. Chromatographic conditions should allow separation of the solvent, the ~~heptane~~ internal standard (I.S.), and at least some of the fuel peaks.

11. Record the signal on a strip chart recorder and integrate the peaks.

12. Make a preliminary estimate of the nature of the hydrocarbon in the soil and its concentration (see CALCULATIONS, below).

13. Run a Blank using the ~~carbon disulfide~~ solution prepared in Step 1. Record and integrate.

14. Prepare standards of gasoline and/or diesel fuel in soil known to be free of hydrocarbon contamination. Make them up in concentrations comparable to those found in Step 12. Carry them through Steps 2. to 11.

NOTES

Note 1. CAUTION Carbon disulfide is highly flammable and toxic. Avoid breathing vapors. Avoid skin contact. Carry out all operations with open vessels of carbon disulfide in a fume hood. Refer to manufacturer's Material Information Bulletin for additional safety information.

Note 2. 100 ml of the carbon ~~disulfide~~ solution will be sufficient for up to 19 soil samples and standards. Greater or smaller amounts can be prepared depending on need. Keep the ratio of heptane to carbon disulfide the same.

Note 3. N-heptane is a component of gasoline and other hydrocarbon mixtures. It is added here as an internal standard in sufficient quantity so that its concentration in the final extract will be much higher than any heptane extracted from the soil.

Note 4. The water is added to the sample to facilitate mixing and to provide a liquid for displacing the ~~carbon disulfide~~ from the soil.

CH₂Cl₂

CALCULATIONS

0.312

hexadecane - CH₂Cl₂ standard:
1 ml hexadecane in
100 ml CH₂Cl₂ or
(put in 1 ml)

1. The carbon disulfide - heptane solution prepared in Step 1, PROCEDURE, contains 34.2 mg heptane in 5.00 mL. This is the internal standard weight, W_{IS}. The weight of soil, in grams, from Step 2 is the sample weight, W_{SAMP}. Estimate the area of the I.S. from the integration of Step 11. This is A_{IS}. Estimate the area of the hydrocarbon from the integration. This is A_{SAMP}. Use the Blank run from Step 13 to help estimate A_{SAMP}.

2. Make a preliminary calculation of the amount of hydrocarbon in the soil sample.

$$\frac{A_{SAMP} \times W_{IS}}{A_{IS} \times W_{SAMP}} \times 1000 = \text{ppm hydrocarbon PRELIM}$$

3. This preliminary calculation, coupled with qualitative identification of the hydrocarbon product, may suffice for decision making. Depending on the chromatographic conditions, the preliminary concentration will be approximately 50% - 90% of the true value. Careful standardation of the method may not be warranted in every case.

4. If more accurate calibration of the method is necessary, plot the ratio of A_{SAMP}/A_{IS} for each of the standards chromatographed in Step 14, PROCEDURE, vs. ppm hydrocarbon in the standards. Compare the A_{SAMP}/A_{IS} ratio of unknown samples to this calibration curve for quantitation.