Analyte:	Tetrachloronaphthalene	Method No.: S130
Matrix:	Air	Range: 0.912-4.04 mg/cu m
OSHA Standard:	2 mg/cu m - skin	Precision ($\overline{CV}_T$): 0.097
Procedure:	Filter and bubbler collection, iso-octane extraction, GC	Validation Date: 5/9/75

1. Principle of the Method

1.1 A known volume of air is drawn through a glass fiber filter connected in series to a midget bubbler containing 15 ml of iso-octane to collect the analyte.

1.2 The filter and the contents in the midget bubbler are transferred to a 20-ml scintillation vial.

1.3 An aliquot from the scintillation vial is analyzed by gas chromatography.

1.4 The total area of the peaks from the sample is determined and compared with areas obtained from standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.912-4.04 mg/cu m at an atmospheric temperature and pressure of 22°C and 760 mm Hg, using a 100-liter sample. The probable useful range of this method is 0.2-6 mg/cu m.

2.2 The upper limit of the range of the method is dependent on the capacity of the glass fiber filter connected in series to the midget bubbler and the capacity of the midget bubbler. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used.

3. Interferences

3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.912-4.04 mg/cu m was 0.097. This value corresponds to a standard deviation of 0.19 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.

4.2 A collection efficiency of 1.00 was determined for the collection medium, thus, no bias was introduced in the sample collection step and no correction for collection efficiency is necessary. There was also no bias in the sampling and analytical method for which an analytical method recovery correction was made. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 Collected samples are analyzed by means of a quick, instrumental method

5.2 A disadvantage of the method is the evaporation of iso-octane in the midget bubbler. The bubbler must be refilled periodically whenever the liquid level is lowered by an appreciable amount.

5.3 Another disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.

5.4 Tetrachloronaphthalene is a mixture of isomers. Under the gas chromatographic conditions used for validation, an "envelope" of peaks was analyzed. The quantitation of area is difficult unless an integrator is used.

5.5 The precision of the method is limited by the reproducibility of the pressure drop across the filter and bubbler. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one filter/bubbler combination only.

5.6 Scintillation vials are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the vials during shipping.

6. Apparatus

6.1 The sampling unit for the collection of personal air samples for the determination of tetrachloronaphthalene has the following components:

6.1.1 The filter unit consisting of the filter media (Section 6.2) and a polystyrene 37-mm two-piece cassette filter holder connected in series with a midget bubbler (Section 6.3). Do not use Tenite filter holders.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5%. The sampling pump is protected from splashover or solvent condensation by a 5-cm long by 6-mm I.D. glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.

6.1.3 Thermometer.

6.1.4 Manometer.

6.2 Glass fiber filter, Type A with a 37-mm diameter. The filter is held in the two-piece cassette filter holder. A backup pad should not be used.

6.3 A glass midget bubbler containing 15 ml of the collection medium (Section 7.3).

6.4 Scintillation vials, 20 ml. Teflon cap liners (22-mm) should be used for proper seal. Add 15 ml of distilled water into each vial and mark the liquid level. Pour out the water and dry each vial.

6.5 Gas chromatograph equipped with an electrolytic conductivity detector (Tracor or equivalent). The system includes an in-line vent between the exhaust end of the GC column and the reduction furnace, a quartz furnace operated in the reductive mode, an electrolytic conductivity cell, and a conductivity bridge.

6.6 Column (5-ft long X 1/8-in O.D. glass) packed with 5% SE-30 on 80/100 mesh, acid washed DMCS Chromosorb W.

6.7 An electronic integrator or some other suitable method for measuring peak areas.

6.8 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions, and 25-microliter for making GC injections.

6.9 Volumetric flasks: 15-ml, and other convenient sizes for making standard solutions.

6.10 Pipets of convenient sizes.

6.11 Tweezers.

7. Reagents

7.1 Tetrachloronaphthalene, reagent grade.

7.2 Benzene, reagent grade.

7.3 Iso-octane, nanograde.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis as well as the scintillation vials should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Sampling Pump. Each personal sampling pump must be calibrated with a representative filter cassette and bubbler in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples.

8.3.1 Assemble the filter in the two-piece filter cassette holder and close firmly.

8.3.2 Pipet 15 ml of the collection medium (Section 7.3) into each midget bubbler and mark the liquid level. The liquid level in the bubbler must be checked frequently. If the liquid level is lowered by an appreciable amount (to less than 10 ml) from evaporation, the bubbler must be refilled with additional iso-octane. The final refilling of iso-octane into the bubbler should be done at approximately 15 minutes before the end of sampling. The final volume of the solution at the end of sampling should be 12 ml or less.

8.3.3 Remove the cassette plugs and attach the outlet of the filter cassette to the inlet arm of the midget bubbler using a short piece of flexible tubing. Connect the outlet arm of the midget bubbler with a 5-cm glass splashover tube (6-mm I.D.) containing the glass wool plug, then to the personal sampling pump, using short pieces of flexible tubing. The bubbler must be maintained in a vertical position during sampling.

8.3.4 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.5 A sample size of 100 liters is recommended. Sample at a flow rate of 1.3 liters per minute. The flow rate should be known with an accuracy of ±5%.

8.3.6 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.7 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.8 After sampling remove the bubbler stem and tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Rinse the bubbler stem with 1 ml of iso-octane into the midget bubbler.

8.3.9 Transfer the contents of the midget bubbler to the scintillation vial which has been marked at 15 ml. Rinse the bubbler with 2 ml of iso-octane, adding the rinse to the vial. Bring the volume in the vial to the 15-ml mark with iso-octane.

8.3.10 The glass fiber filter should be removed from the cassette filter holder and placed in the scintillation vial. Care must be taken to handle the filter only with clean tweezers. Cap the scintillation vials with appropriate caps with Teflon liners.

8.3.11 Carefully record the sample identity and all relevant sampling data.

8.3.12 With each batch of ten samples submit one filter and bubbler from the same lot of filters and bubblers which was used for sample collection and which are subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.

8.3.13 The scintillation vials in which the samples are stored should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Each sample is analyzed separately. Before injection of the sample into the GC, swirl the contents in the vials for 5 minutes.

8.4.2 Appropriate blanks must be analyzed at the same time as the samples.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 150 ml/min nitrogen carrier gas flow

2. 150 ml/min hydrogen gas flow to furnace

3. 760°C furnace temperature

4. 225°C transfer temperature

5. 250°C vent temperature

6. 185°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of an aliquot of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 25-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 1.0 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 15-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.0 microliter to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 14.9-15.0 microliters in the barrel of the syringe. The gas chromatograph is equipped with a valve to vent the solvent peak after it passes through the GC column, but before it enters a reduction furnace. Since a 15-microliter aliquot is likely to cause malfunction of the electrolytic conductivity cell, the valve should be opened when injection is made and should be closed after the solvent (iso-octane) has been vented and before the analyte is eluted. Under the conditions above (Section 8.4.3), it was found that 20 seconds was adequate to elute the solvent. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The areas of the sample peaks are measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9. The peaks are not resolved, and therefore the total area of the envelope of peaks is measured as a single area.

8.5 Determination of Analytical Method Recovery

8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the analyte. The analytical method recovery (A.M.R.) should be determined over the concentration range of interest.

8.5.2 Procedure for determining analytical method recovery. A known amount of benzene solution containing 50 mg/ml of tetrachloronaphthalene is added to a representative glass fiber filter and allowed to air dry. The analyte is then extracted from the filter with 15 ml of iso-octane for one hour and analyzed as described in Section 8.4. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) are dosed accordingly. A parallel blank filter is also treated in the same manner except that no sample is added to it. All filters are extracted in 15 ml iso-octane for one hour and analyzed as described in Section 8.4.

Three standards are prepared by injecting the same amount of analyte into 15 ml of iso-octane with the same syringe used in the preparation of the dosed filters and are analyzed at the same time.

Analytical method recovery (A.M.R.) equals the weight in mg found divided by the weight in mg added to the filter, or

$$\text{A. M. R.} = \frac{\text{Weight found (mg)}}{\text{Weight added (mg)}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/15 ml iso-octane, because samples are extracted in this amount of iso-octane. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/15 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of day-to-day variations and variations during the same day of the electrolytic conductivity detector response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each envelope of peak area from the standard curve. No volume correction is needed, because the standard curve is based on mg/15 ml of iso-octane, and the volume of sample injected is identical to the volume of the standards injected.

10.2 A correction for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in sample filter and bubbler
mg blank = mg found in blank filter and bubbler

10.3 Divide the total weight by the analytical method recovery (A.M.R.) to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{A.M.R.}}$$

10.4 The concentration of the analyte in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.3) X 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

11. Reference

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.