IX. APPENDIX I

SAMPLING AND ANALYSIS FOR SELECTED KETONES

The following method for 12 selected ketones is adapted from NIOSH methods validated for 11 of the compounds [114,115]. Mention of company name or product does not constitute endorsement by NIOSH.

Principle of the Method

(a) A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

(b) The charcoal in the tube is transferred to a small, stoppered glass sample container and desorbed with carbon disulfide.

(c) An aliquot of the desorbed sample is injected into a gas chromatograph.

(d) The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

Range and Sensitivity

(a) This method was validated for the individual ketones over the range presented in Table IX-1. An atmospheric temperature and pressure of approximately 25 C and 761 mmHg and a sample size of 10-12 liters were used. The method is capable of measuring much lower concentrations, but they have not been validated. Methyl n-butyl ketone, for example, is measurable at a concentration of 4 mg/cu m provided desorbing efficiency is

TABLE IX-1

RANGE, COEFFICIENTS OF VARIATIONS, AND STANDARD DEVIATION OF THE RECOMMENDED SAMPLING AND ANALYTICAL METHOD FOR KETONES

Ketone	Validated Range (mg/cu m)	Probable Range (mg/cu m)	Coefficient of Variation	Standard Deviation*	Deviation From True Values	Reference
Acetone	1,200-4,500	350-5,000	0.082	4.1%**	-2%	114
Methyl ethyl ketone	380-1,240	70-1,500	0.072	46 mg/cu m	+9%	114
Methyl n-propyl ketone	395-1,570	70-2,100	0.063	21 mg/cu m	-1.3%	114
Methyl n-butyl ketone	166-790	40-1,200	0.053	22 mg/cu m	-0.5%	115
Methyl n-amyl ketone	200-925	50-1,000	0.0660	15.7 mg/cu m	+2%	114
Methyl isobutyl ketone	208-836	40-1,230	0.064	17 mg/cu m	-4.8%	114
Methyl isoamyl ketone	NO DATA AVAILABLE					
Diisobutyl ketone	145-582	30-1,000	0.070	20.3 mg/cu m	-1.4%	115
Cyclohexanone	98-392	10-500	0.062	7.4 mg/cu m	-6.3%	114
Mesityl oxide	45-210	10-300	0.0708	7.8 mg/cu m	+7%	114
Diacetone alcohol	140-510	24-750	0.104	24.1 mg/cu m	-11.9%	114
Isophorone	68-283	2-400	0.058	8 mg/cu m	+5%	115

*At current Federal standard
**Relative standard deviation

adequate since the lower limit of detection for the NIOSH validated method has been stated as 0.01 mg/cu m [146]. Desorption efficiency must be determined over the actual range of the samples.

(b) The useful range of the sampling method depends largely on the adsorptive capacity of the charcoal tube. The total amount of ketone collected will vary with the sampling rate and with the concentrations of ketones and other substances, particularly water vapor, in the air. Experimental results on breakthrough are listed in Table IX-2 and were determined with a relative humidity of less than 15% and at normal conditions. If a particular atmosphere is suspected of containing a large amount of ketone, a smaller sample volume should be collected.

Interference

(a) When the amount of water in the air is so great that condensation actually occurs in the charcoal tube, ketone vapors will not be trapped efficiently.

(b) When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

(c) It must be emphasized that any compound that has the same retention time as the ketone at the operating conditions described in this method will interfere. Hence, retention time data on a single column, or even on a number of columns, cannot always be considered proof of chemical identity.

(d) If interference is known to occur with the analysis in question, separation conditions (column packing, temperature, etc) must be changed to circumvent the problem.

Precision and Accuracy

The coefficients of variation, standard deviations, and deviations from "true" values for the combined sampling and analytical method are listed in Table IX-1. The standard deviation at the present Federal standard is also reported. The data in Table IX-1 for mesityl oxide, methyl n-butyl ketone, methyl n-amyl ketone, and diacetone alcohol are based on experiments using an internal standard.

Advantages and Disadvantages of the Method

(a) The sampling device is small and portable and involves no liquids. Analytical interferences are usually minimal, and most of those that do occur can be eliminated by altering the chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. In some cases, by adjusting chromatographic conditions, the method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample, provided that each substance can be efficiently desorbed with the same desorbing medium.

TABLE IX-2

BREAKTHROUGH DATA IN CHARCOAL TUBE SAMPLING OF THE KETONES

Ketone	Amount of Ketone in 1st Section (mg)	Influent Test Atmosphere (mg/cu m)	Sampling Rate (liters/min)	Breakthrough Time* (min)	Reference
Acetone	18	4,300	0.195	22	114
Methyl ethyl ketone	19	1,260	0.17	86	114
Methyl n-propyl ketone	27	1,450	0.19	100	114
Methyl n-butyl ketone	35	790	0.187	240**	115
Methyl n-amyl ketone	15	925	0.2	>180**	114
Methyl isobutyl ketone	20	1,145	0.19	91.7	114
Diisobutyl ketone	25	582	0.20	219	115
Cyclohexanone	26***	-	-	-	114
Mesityl oxide	9.6	210	0.2	240	114
Diacetone alcohol	24	507	0.2	>240**	114
Isophorone	13	283	0.19	>240**	115

*When concentration of ketone in effluent reaches 5% of that in influent
**No breakthrough in stated time
***In 1st section when breakthrough occurred

(b) One disadvantage of the method is that the amount of sample that can be taken is limited by the mass of ketone that the tube will hold before overloading. This sample size is dependent on the types and concentrations of the contaminants in the workplace air. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, sample loss must be suspected.

(c) The precision of the method is limited by the reproducibility of the pressure drop across the tubes. If the pump is calibrated for one tube only, variations in pressure drop from tube to tube will result in different flowrates and cause volumes to be imprecise.

Apparatus

(a) An approved and calibrated personal sampling pump with a flow that can be determined to within 5% at the recommended flowrate.

(b) Charcoal tubes: glass tube with both ends flame-sealed, 7 cm long with a 6-mm outer diameter and a 4-mm inner diameter, containing two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The absorbing front section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in the front of the tube. The pressure drop across the tube must be less than 1 inch of mercury at a flowrate of 1 liter/ minute.

(c) Gas chromatograph equipped with a flame-ionization detector.

(d) Chromatographic column:

(1) 20-feet x 1/8-inch stainless steel, packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS (acid-washed dimethylchlorosilated) for methyl n-butyl ketone.

(2) 4-feet x 1/4-inch stainless steel, packed with 50/80 mesh Porapak, Type Q, for acetone.

(3) 10-feet x 1/8-inch stainless steel, packed with 10% FFAP on 80/100 mesh Chromosorb W DMCS, for the other 10 ketones.

(e) An electronic integrator or some other suitable method for measuring peak areas.

(f) One-milliliter glass sample containers with glass stoppers or Teflon-lined caps.

(g) Microliter syringes: 10-μl and other convenient sizes for making standards.

(h) Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

(i) Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

Reagents

(a) Chromatographic quality carbon disulfide (containing 5% 2-propanol for diacetone alcohol analysis).

(b) Ketone, reagent grade.

(c) Purified nitrogen.

(d) Prepurified hydrogen.

(e) Filtered compressed air.

(f) n-Tridecane (99+%) for use as internal standard.

(g) n-Heptane, reagent grade.

Procedure

(a) Cleaning of Equipment. Detergent wash all glassware used for the laboratory analysis and rinse thoroughly with tapwater and distilled water.

(b) Calibration of Personal Pumps. Calibrate each personal pump with a representative charcoal tube in line as shown in Figure XI-1. This will minimize errors associated with uncertainties in the sample volume collected.

(c) Collection and Shipping of Samples

(1) Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

(2) Use the smaller section of charcoal as a backup and position it nearest the sampling pump.

(3) Place the charcoal tube in a vertical direction during sampling to minimize channeling through the charcoal.

(4) Do not pass air being sampled through any hose or tubing before entering the charcoal tube.

(5) A maximum sample size of 10-12 liters is recommended. This size can be attained by sampling at a rate of 0.20 liter/minute. The flowrate should be known with an accuracy of at least 5%.

(6) Record the temperature and pressure of the atmosphere being sampled.

(7) Cap the charcoal tubes with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

(8) Handle at least one tube in the same manner as the sample tube (break, seal, and transport), but do not draw air through this tube. Label this tube as a blank.

(9) Pack capped tubes tightly before they are shipped to minimize tube breakage during shipping.

(10) Submit a sample of the bulk material to the laboratory in a glass container with a Teflon-lined cap. Do not transport this sample in the same container as the charcoal tubes.

(d) Analysis of Samples

(1) Preparation of Samples. Sample tubes will be received opened but protected by plastic caps. Remove the plastic cap from the front section, discard the glass wool in front of the charcoal, and transfer the charcoal in the first (larger) section to a 1-ml stoppered sample container. Remove and discard the separating section of foam; transfer the second section to another stoppered container. Analyze these two sections separately.

(2) Desorption of Samples. Prior to analysis, pipet 0.5 ml of carbon disulfide (1.0 ml for mesityl oxide, methyl n-butyl ketone, diacetone alcohol, and methyl n-amyl ketone analysis) into each sample container. For the internal standard method, use a 0.1% solution of the internal standard in the eluent. Tests have indicated that desorption is

complete in 30 minutes if the sample is stirred occasionally during this period. If an automatic sample injector is used, cap the sample vials as soon as the solvent is added to minimize volatilization.

EXTREME CAUTION MUST BE EXERCIZED AT ALL TIMES WHEN USING CARBON DISULFIDE BECAUSE OF ITS HIGH TOXICITY AND FIRE AND EXPLOSION HAZARDS. IT CAN BE IGNITED BY HOT STEAM PIPES. ALL WORK WITH CARBON DISULFIDE MUST BE PERFORMED UNDER AN EXHAUST HOOD.

(3) Chromatograph Conditions. The typical operating conditions for the gas chromatograph for each ketone are listed in Table IX-3.

(4) Injection. The first step in the analysis is the injection 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, possibly using a syringe guide for ease of performance. First flush the 10-μl syringe with solvent several times to wet the barrel and plunger. Draw 3 μl of solvent into the syringe to increase the accuracy and reproducibility of the injected sample volume. Remove the needle from the solvent, and pull the plunger back about 0.2 μl to separate the solvent flush from the sample with a pocket of air to be used as a marker. Immerse the needle in the sample, and withdraw a 5-μl aliquot, taking into consideration the volume of the needle, since the sample in the needle will be completely

TABLE IX-3

TYPICAL CHROMATOGRAPH CONDITIONS FOR KETONES

Ketone	Gas Flow (ml/min)			Temperature (C)			Reference
	Carrier Nitrogen	Hydrogen*	Air*	Injector	Detector	Column	
Acetone	50 at 60 psig	65 at 24 psig	500 at 50 psig	175	200	125	114
Methyl ethyl ketone	"	"	"	100	200	50	114
Methyl n-propyl ketone	"	"	"	190	250	60	114
Methyl n-butyl ketone	30 at 60 psig	35 at 25 psig	400 at 60 psig	225	250	80	115
Methyl n-amyl ketone	30 at 80 psig	30 at 50 psig	300 at 50 psig	200	300	120	114
Methyl isobutyl ketone	50 at 60 psig	65 at 24 psig	500 at 50 psig	260	193	65	114
Methyl isoamyl ketone	"	"	"	200	300	120	114
Diisobutyl ketone	50 at 60 psig	65 at 24 psig	500 at 50 psig	230	241	71	115
Cyclohexanone	"	"	"	220	255	110	114
Mesityl oxide	30 at 80 psig	30 at 50 psig	300 at 50 psig	200	300	120	114
Diacetone alcohol	"	"	"	200	300	120	114
Isophorone	50 at 60 psig	65 at 24 psig	500 at 50 psig	255	250	167	115

*Flow to detector

injected. After removing the needle from the sample and prior to injection, pull the plunger back 1.2 μl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 μl in the barrel of the syringe. Make duplicate injections of each sample and standard. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case, 2-μl injections are satisfactory.

(5) Measurement of Area. Measure the area of the sample peak with an electronic integrator or some other suitable form of area measurement and read preliminary results from a standard curve prepared as discussed below.

(e) Determination of Desorption Efficiency

(1) Importance of Determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process for a given compound, provided the same batch of charcoal is used.

(2) Effect of Time. The amount of cyclohexanone found on the charcoal tubes decreased with time. The storage stability of the other ketones was not tested. Therefore, in determining desorption efficiency for field samples, the spiked tubes should be stored under the same conditions as the field samples (for example, time and temperature of storage should be the same).

(3) Procedure for Determining Desorption Efficiency. Measure an amount of activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) into a 7-cm, 4-mm inner diameter glass tube, flame-sealed at one end. This charcoal must be from the batch used in obtaining the samples, and it can be obtained from unused charcoal tubes. Cap the open end with Parafilm. Inject a known amount of the ketone directly into the activated charcoal with a microliter syringe, and cap the tube with more Parafilm. For mesityl oxide analysis, inject an 8% stock solution of mesityl oxide in n-heptane in the desired amount. For diacetone alcohol, use a 600 mg/ml stock solution of the analyte in n-heptane. In experiments conducted to validate the method, the amount injected was approximately equivalent to that present in a 10- or 12-liter sample at the selected level.

Prepare six tubes, each containing an amount of ketone that would be expected in a 10- to 12-liter sample of air at 0.5X, 1.0X, and 2.0X the recommended workplace environmental limit specified for the ketone of interest in Chapter I. Allow these tubes to stand at least overnight to assure complete sorption of the analyte onto the charcoal. These tubes are referred to as the samples. Treat a parallel blank tube in the same manner but add no ketone to it. Desorb and analyze the sample and blank tubes in exactly the same manner as the sampling tube.

Prepare two or three standards by injecting the same volume of compound into 0.5 ml (or 1.0 ml) of carbon disulfide. Analyze these standards with the samples.

The desorption efficiency equals the average weight in milligrams recovered from the tube divided by the weight in milligrams added to the tube, or

$$\text{Desorption Efficiency} = \frac{\text{average weight (mg) recovered}}{\text{weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. Use this curve to correct for adsorption losses.

Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml (or mg/1.0 ml as appropriate) of carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the ketone is used to convert mg into μl for easy measurement with a microliter syringe. When using an internal standard, prepare a final concentration of 0.1% standard in the desorbent. Prepare a series of standards, varying in concentration over the range of interest, and analyze them under the same gas-chromatographic conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area; a linear response is expected with the ketones.

> Note: If an internal standard is not 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 known day-to-day variations and variations during the same day of the flame-ionization detector response. In the case of the internal standard method, plot concentration versus the ratio of peak area of ketone to peak area of the internal standard.

Calculations

(a) Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml (or mg/1.0 ml) of carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

(b) Corrections for the blank must be made for each sample:

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

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

Use a similar procedure for the backup sections.

(c) Add the weights found in the front and backup sections to get the total weight in the sample.

(d) Read the desorption efficiency from the curve for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the total mg/sample:

$$\text{corrected mg/sample} = \frac{\text{total weight}}{\text{desorption efficiency}}$$

(e) The concentration of the ketone in the sampled air can be expressed in mg/cu m:

$$\text{mg/cu m} = \frac{\text{total mg} \times 1{,}000 \text{ (liters/cu m)}}{\text{air volume sampled (liters)}}$$

(f) Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{FW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mmHg) of air sampled

T = temperature (C) of air sampled

24.45 = molar volume (liters/mole) at 25 C and 760 mmHg

FW = formula weight

760 = standard pressure (mmHg)

298 = standard temperature (K)