Method number:	PV2019
Target concentration:	1.5 ppm (10 mg/m^3)
Procedure:	Samples are collected by drawing a known volume of air through a charcoal tube. Samples are desorbed with 1 mL of 1:99 dimethyl formamide:carbon disulfide (DMF:CS_2) for 30 minutes with shaking and then analyzed by gas chromatography using a flame ionization detector (GC-FID).
Recommended air volume and sampling rate:	100 minutes at 0.2 L/min (20 L)
Reliable quantitation limit:	0.012 ppm (0.084 mg/m^3)
Status of method:	Partially Evaluated Method. This method has been subjected to established evaluation procedures, and is presented for information and trial use.

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1 General Discussion

1.1 Background

1.1.1 History

Samples collected on charcoal tubes were received by the Salt Lake Technical Center (SLTC) requesting the analysis for dimethyl adipate (DMAD). A desorption study using carbon disulfide showed non-linear desorption, with the recoveries dependent on the concentration spiked, 55% for 21.3 µg DMAD, and 83% for 213 µg DMAD. A solution of 1:99 dimethyl formamide:carbon disulfide was explored next and found to give good recoveries, averaging 95.1%. The retention and storage studies were performed next, and found to give good recoveries.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.) (Ref. 5.1)

DMAD is a human skin, eye, and mucous membrane irritant. Worker exposure by inhalation or through skin contact has been observed to cause blurred vision. There is no PEL or TLV for DMG, but DuPont recommends an AEL (Acceptable Exposure Limit) of 1.5 ppm or 10 mg/m^3 for an 8 hour TWA. Animal toxicology studies with a mixture of dimethyl glutarate, dimethyl adipate, and dimethyl succinate indicates that the mixture is a mild to severe skin irritant, depending on the animal tested. The mixture is an eye and mucous membrane irritant in rats and rabbits. Rats exposed to 60 ppm for 4 hours had transient corneal opacity and transient increases in the distance from the cornea to the anterior surface of the lens of the eye, which probably caused blurred vision. The LD_{50} in rats for intraperitoneal exposure was 1809 µL/kg.

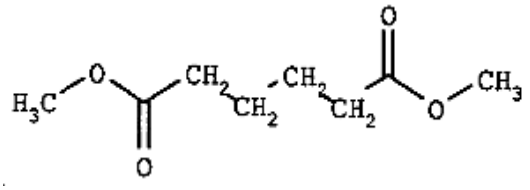
1.1.3 Workplace exposure (Ref. 5.1 and 5.2)

DMAD is used in paints, lacquers, varnishes, in plasticizers for cellulose type resins, and in paint strippers.

1.1.4 Physical properties and other descriptive information (Ref. 5.1, 5.2, and 5.3)

Synonyms:	Adipic acid, dimethyl ester; Dimethyl hexanedioate; Hexanedioic acid, dimethyl ester; Methyl adipate
CAS number:	627-93-0
IMIS:	D649
RTECS:	AV1645000
Molecular weight:	174.22
Flash point:	107 °C (225 °F) (cc)
Boiling point:	115 °C
Melting point:	10.3 °C
Odor:	sweet
Color:	clear liquid
Autoignition temperature:	360 °C (680 °F)
Density:	1.060 (d^{20}_4)
Molecular formula:	$C_8H_{14}O_4$

Structural formula:



The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppm are referenced to 25 °C and 101.3 kPa (760 mmHg).

1.2 Limit defining parameters

1.2.1 Detection limit of the overall procedure (DLOP)

The detection limit of the overall procedure is 0.501 µg per sample (0.0035 ppm or 0.0251 mg/m^3). This is the amount of analyte spiked on the sampler that will give a response that is significantly different from the background response of a sampler blank.

The DLOP is defined as the concentration of analyte that gives a response (Y_{DLOP}) that is significantly different (three standard deviations (SD_{BR})) from the background response (Y_{BR}).

$$Y_{DLOP} - Y_{BR} = 3(SD_{BR})$$

The direct measurement of Y_{BR} and SD_{BR} in chromatographic methods is typically inconvenient and difficult because Y_{BR} is usually extremely low. Estimates of these parameters can be made with data obtained from the analysis of a series of samples whose responses are in the vicinity of the background response. The regression curve obtained for a plot of instrument response versus concentration of analyte will usually be linear. Assuming SD_{BR} and the precision of data about the curve are similar, the standard error of estimate (SEE) for the regression curve can be substituted for SD_{BR} in the above equation. The following calculations derive a formula for the DLOP:

$$SEE = \sqrt{\frac{\sum \left(Y_{obs} - Y_{est}\right)^2}{\left(n - k\right)}}$$

Yobs = observed response
Yest = estimated response from regression curve
n = total number of data points
k = 2 for a linear regression curve

At point Y_{DLOP} on the regression curve

$$Y_{DLOP} = A(DLOP) + Y_{BR}$$

A = analytical sensitivity (slope)

Therefore:

$$DLOP = \frac{\left(Y_{DLOP} - Y_{BR}\right)}{A}$$

Substituting 3(SEE) + Y_{BR} for Y_{DLOP} gives

$$DLOP = \frac{3(SEE)}{A}$$

The DLOP is measured as mass per sample and expressed as equivalent air concentrations, based on the recommended sampling parameters. Ten samplers were spiked with equal descending increments of analyte, such that the lowest sampler loading was 1.06 µg/sample. This is the amount, when spiked on a sampler, that would produce a peak approximately 10 times the background response for the sample blank. These spiked samplers, and the sample blank were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (A and SEE) for the calculation of the DLOP. Values of 132.5 and 22.10 were obtained for A and SEE respectively. DLOP was calculated to be 0.501 µg/sample (0.0035 ppm or 0.0251 mg/m^3).

Table 1.2.1
Detection Limit of the Overall Procedure

mass/sample µg	area counts (V-s)
0	0
1.06	137
2.13	279
3.19	451
4.25	592
5.32	721
6.38	863
7.44	1019
8.50	1124
9.57	1238
10.6	1437

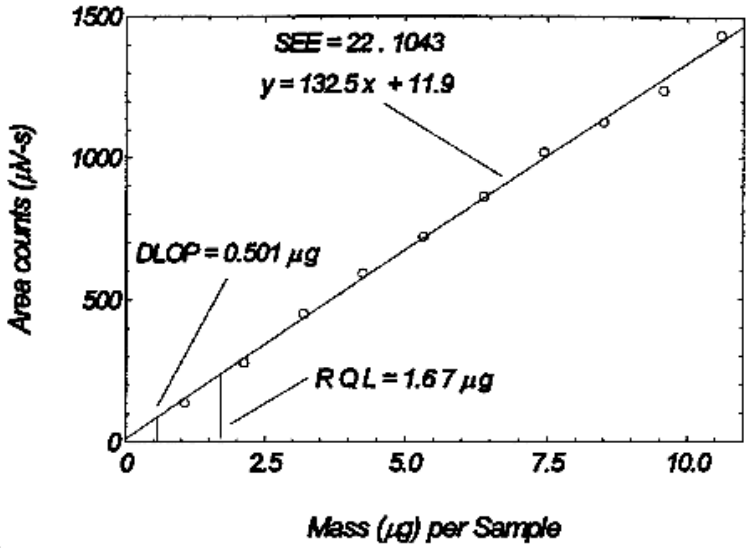


Figure 1.2.1 Plot of data to determine the DLOP and RQL.

1.2.2 Reliable quantitation limit (RQL)

The reliable quantitation limit is 1.67 µg per sample (0.012 ppm). This is the amount of analyte spiked on a sampler that will give a signal that is considered the lower limit for precise quantitative measurements.

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line data obtained for the calculation of the DLOP (Section 1.2.1), providing at least 75% of the analyte is recovered. The RQL is defined as the concentration of analyte that gives a response (Y_{RQL}) such that

$$Y_{RQL} - Y_{BR} = 10(SD_{BR})$$

Therefore:

$$RQL = \frac{10(SEE)}{A}$$

RQL = 1.67 µg per sample (0.011 ppm)

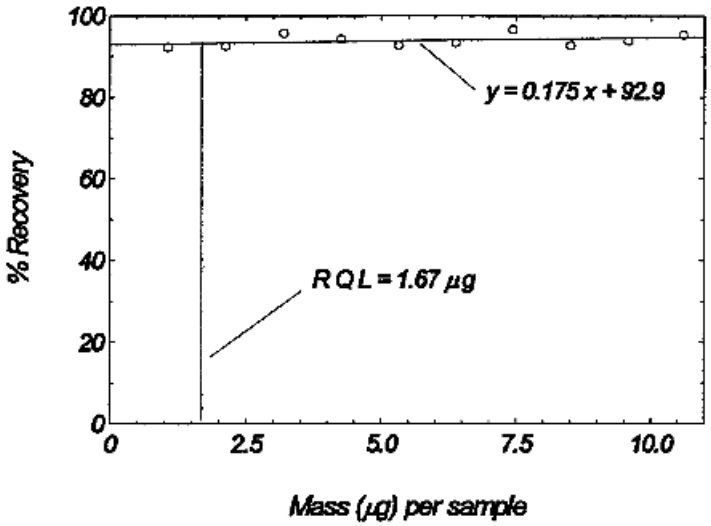


Figure 1.2.2 Plot of data to determine the RQL.

Table 1.2.2
Reliable Quantitation Limit

mass/sample µg	mass recovered µg	% recovered
1.06	0.977	92.2
2.13	1.97	92.5
3.19	3.06	95.9
4.25	4.01	94.4
5.32	4.93	92.7
6.38	5.95	93.3
7.44	7.19	96.6
8.50	7.89	92.8
9.57	8.99	93.9
10.6	10.1	95.3

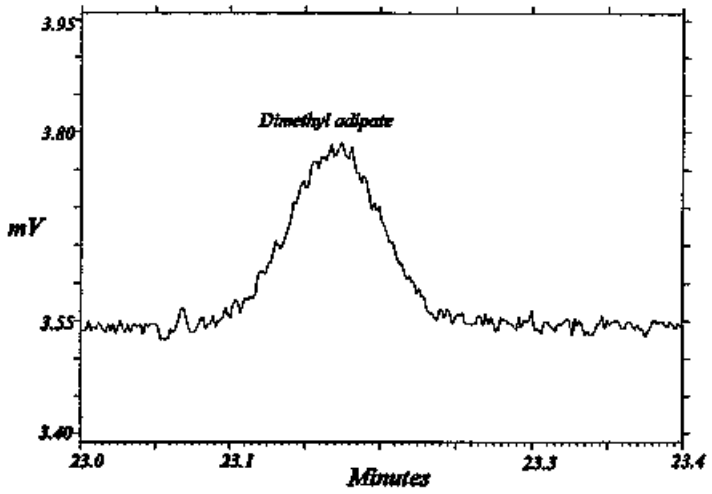


Figure 1.2.3 Chromatogram of the RQL.

2 Sampling Procedure

2.1 Apparatus

2.1.1 Samples are collected using a personal sampling pump calibrated, with the sampling device attached, to within ±5% of the recommended flow rate.

2.1.2 Samples are collected with glass sampling tubes (7 cm x 4 mm i.d. x 6 mm o.d.) packed with two sections of coconut shell charcoal. The front section contains 100 mg and the back section contains 50 mg of charcoal, lot 120. The sections are held in place with glass wool plugs and are separated by a urethane foam plug. For this evaluation, commercially prepared sampling tubes were purchased from SKC Inc., (Eighty Four PA) catalog No. 226-01, Lot 120.

2.2 Technique

2.2.1 Immediately before sampling, break off the ends of the sampling tube. All tubes should be from the same lot.

2.2.2 Attach the sampling tube to the pump with flexible tubing. It is desirable to utilize sampling tube holders which have a protective cover to shield the employee from the sharp, jagged end of the sampling tube. Position the tube so that sampled air passes through the front section of the tube first.

2.2.3 Air being sampled should not pass through any hose or tubing before entering the sampling tube.

2.2.4 Attach the sampler vertically with the front section pointing downward, in the worker's breathing zone, and positioned so it does not impede work performance or safety.

2.2.5 After sampling for the appropriate time, remove the sample and seal the tube with plastic end caps. Wrap each sample end-to-end with a Form OSHA-21 seal.

2.2.6 Submit at least one blank sample with each set of samples. Handle the blank sample in the same manner as the other samples except draw no air through it.

2.2.7 Record sample volumes (in liters of air), sampling time, and flow rate for each sample, along with any potential interference.

2.2.8 Ship any bulk samples separate from the air samples.

2.2.9 Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples in a refrigerator.

2.3 Desorption efficiency

The desorption efficiencies of DMAD were determined by liquid spiking the charcoal tubes with the analytes at 0.1 to 2 times the target concentration. The loadings on the tubes were 21.2, 106, 212, and 424 µg of DMAD. These samples were stored overnight at ambient temperature and then desorbed with 1 mL of 1:99 DMF:CS2 with 0.25 µL/mL p-cymene internal standard, and analyzed by GC-FID. The average desorption efficiency over the studied range was 95.1%.

Table 2.3
Desorption Efficiency of DMAD

tube #	% recovered			
	0.1x 21.2 µg	0.5x 106 µg	1.0x 212 µg	2.0x 424 µg
1	94.7	96.6	96.2	93.3
2	93.3	94.1	93.9	94.0
3	95.1	94.2	95.7	96.5
4	93.6	95.4	96.9	95.4
5	93.9	95.0	96.2	95.6
6	94.3	95.8	97.2	96.5
average	94.2	95.2	96.0	95.2

overall average = 95.1
standard deviation = ±1.20

2.4 Retention efficiency

The glass wool in front of the front section was pulled towards the newly opened end, so that it was not in contact with the charcoal in the tube. The glass wool was spiked with 424 µg (3.0 ppm) DMAD, to check the ability of DMAD to volatilize and to be collected onto the charcoal tube. After spiking the glass wool, the tubes had 20 L humid air (80% RH at 21 °C) pulled through them at 0.2 L/min. They were opened, each section placed into a separate vial, desorbed, and analyzed by GC-FID. The retention efficiency averaged 95.8%. There was no DMAD found on the back sections of the tubes. There was little or no DMAD found on the glass wool, indicating most or all of it was vaporized, and the total recovered indicates most of the vaporized DMAD was collected by the charcoal. The recoveries in the table are not corrected for desorption efficiency.

Table 2.4
Retention Efficiency of DMAD

tube #	% recovered			
	glass wool	front section	back section	total
1	0.0	93.7	0.0	93.7
2	0.0	97.2	0.0	97.2
3	0.0	96.6	0.0	96.6
4	0.0	96.8	0.0	96.8
5	0.0	96.3	0.0	96.3
6	2.1	92.3	0.0	94.4
average				95.8

2.5 Sample storage

The front sections of twelve sampling tubes were each spiked with 424 µg (3 ppm) of DMAD, then six tubes were stored in the refrigerator (-10°C), and the other six tubes were stored at room temperature (23 °C). Twelve more tubes were spiked with 424 µg (3 ppm) of DMAD, and then had 20 liters of humid air (80% RH at 21°C) drawn through them, then six tubes were stored in the refrigerator (-10°C), and the other six tubes were stored at room temperature (23 °C). Three of each type of samples was analyzed after 7 days and the remaining three samples of each type after 14 days. The average recovery over the 14-day storage study was 94.5%.

Table 2.5
Storage Test for DMAD

time (days)	% recovered			
	humid ambient	humid refrigerated	dry ambient	dry refrigerated
7	94.9	90.3	95.5	98.4
7	93.0	93.6	95.7	95.9
7	90.2	95.6	94.6	94.4
14	93.3	94.7	94.2	98.2
14	92.5	90.6	95.8	96.2
14	95.3	94.2	96.2	94.2
average	93.2	93.2	95.3	96.2

overall average = 94.5%

2.6 Recommended air volume and sampling rate.

Based on the data collected in this evaluation, 20 L air samples should be collected at a sampling rate of 0.2 L/min.

2.7 Interferences (sampling)

2.7.1 It is not known if any compounds will severely interfere with the collection of DMAD on the sampling tubes. In general, the presence of other contaminant vapors in the air will reduce the capacity of the charcoal tube to collect DMAD.

2.7.2 Suspected interferences should be reported to the laboratory with submitted samples.

2.8 Safety precautions (sampling)

2.8.1 Attach the sampling equipment to the worker in such a manner that it will not interfere with work performance or safety.

2.8.2 Follow all safety practices that apply to the work area being sampled.

2.8.3 Wear eye protection when breaking the ends of the glass sampling tubes.

3 Analytical Procedure

3.1 Apparatus

3.1.1 The instrument used in this study was a gas chromatograph (GC) equipped with a flame ionization detector (FID), specifically a Hewlett Packard model 5890.

3.1.2 A GC column capable of separating the analyte from any interference. The column used in this study was a 60-m x 0.32-mm i.d. with (0.5 µm d_f DB-WAX) capillary column.

3.1.3 An electronic integrator or some suitable method of measuring peak areas.

3.1.4 Two milliliter vials with PTFE-lined caps.

3.1.5 A 10-µL syringe or other convenient size for sample injection.

3.1.6 Pipettes for dispensing the desorbing solution. A Repipet dispenser was used in this study.

3.1.7 Volumetric flasks, 5-mL or 10 mL and other convenient sizes for preparing standards.

3.2 Reagents

3.2.1 GC grade nitrogen, hydrogen, and air.

3.2.2 Dimethyl adipate, Reagent grade

3.2.3 Carbon disulfide, Reagent grade

3.2.4 Dimethyl formamide, Reagent grade

3.2.5 p-Cymene, Reagent grade (internal standard)

3.2.6 Desorbing solution was 1:99 DMF:carbon disulfide with 0.25 µL/mL p-cymene internal standard.

3.3 Standard preparation

3.3.1 At least two separate stock standards are prepared by diluting a known quantity of DMAD with the desorbing solution of 1:99 DMF:carbon disulfide with 0.25 µL/mL p-cymene internal standard. The concentration of these stock standards was 0.2 µL/mL or 212 µg/mL.

3.3.2 A third standard at a higher concentration was prepared to check the linearity of the calibration. For this study, two analytical standards were prepared at a concentration of 0.2 µL/mL (212 µg/mL), and one at 1 µL/mL (1060 µg/mL) DMAD in the desorbing solution.

3.4 Sample preparation

3.4.1 Sample tubes are opened and the front and back section of each tube are placed in separate 2 mL vials.

3.4.2 Each section is desorbed with 1 mL of the desorbing solution of 1:99 DMF:carbon disulfide with 0.25 µL/mL p-cymene internal standard.

3.4.3 The vials are sealed immediately and allowed to desorb for 30 minutes with constant shaking.

3.5 Analysis

3.5.1 Gas chromatograph conditions.

Injection size: 1 µL

Flow rates	**(mL/min)**
Nitrogen (make-up):	30
Hydrogen (carrier):	2
Hydrogen (detector):	40
Air:	420

Temperatures	**(°C)**
Injector:	200
Detector:	220
Column:	50 °C for 2 min then heat at 10 °C/min to 170 °C hold 12 min

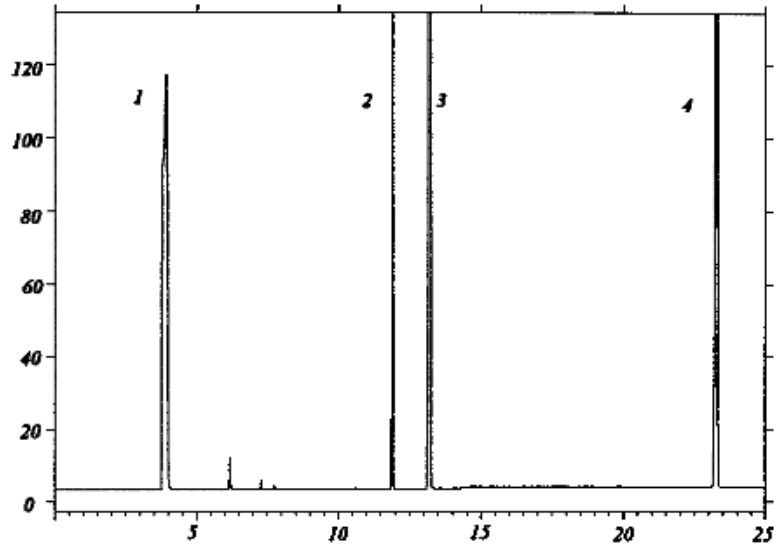


Figure 3.5.1 Chromatogram of an analytical standard at the target concentration. Peak identification: (1) carbon disulfide, (2) p-cymene, (3) DMF, and (4) DMAD.

3.5.2 Peak areas are measured by an integrator or other suitable means.

3.6 Interferences (analytical)

3.6.1 Any compound that produces a response and has a similar retention time as the analyte is a potential interference. If any potential interference were reported, they should be considered before samples are desorbed. Generally, chromatographic conditions can be altered to separate interference from the analyte.

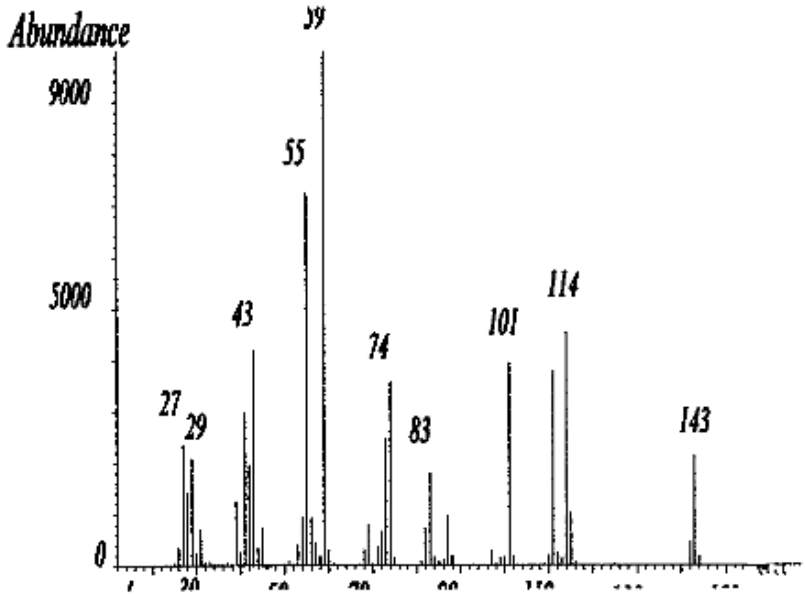


Figure 3.6.1 mass spectra of dimethyl adipate (DMAD).

3.6.2 When necessary, the identity or purity of an analyte peak may be confirmed by GC-mass spectrometer or by another analytical procedure.

3.7 Calculations

3.7.1 The instrument was calibrated with a standard of 212 µg/mL DMAD in the desorbing solution. The linearity of the calibration was checked with a standard of 1060 µg/mL.

3.7.2 If the calibration is non-linear, two or more standards at different concentrations must be analyzed, bracketing the samples, so a calibration curve can be plotted and sample values obtained.

3.7.3 To calculate the concentration of analyte in the air sample the following formulas are used:

$$\text{mass of analyte, } \mu g = \frac{(\mu g / mL)(\text{desorption volume, } mL)}{(\text{desorption efficiency, decimal})}$$

$$\text{moles of analyte} = \frac{(\text{mass of analyte, } \mu g)(1\,g)}{(\text{molecular weight})(10^6\,\mu g)}$$

$$\text{volume of analyte} = (\text{moles of analyte})(\text{molar volume})$$

$$ppm = \frac{(volume\ of\ analyte)(10^6)}{(air\ volume,\ L)}$$

* All units must cancel.

3.7.4 The above equations can be consolidated to the following formula.

$$ppm = \frac{(\mu g / mL)(DV)(24.46)}{(10\ L)(DE)(MW)}$$

μg/mL = concentration of analyte in sample or standard
24.46 = Molar volume (liters/mole) at 25 °C and 760 mmHg.
MW = Molecular weight (g/mole)
DV = Desorption volume, mL
10 L = 10 liter air sample
DE = Desorption efficiency, decimal

3.7.5 This calculation is done for each section of the sampling tube and the results added together.

3.8 Safety precautions (analytical)

3.8.1 Avoid skin contact and inhalation of all chemicals.

3.8.2 Wear safety glasses, gloves, and a lab coat at all times while in the laboratory areas.

4 Recommendations for Further Study

Collection studies need to be performed from a dynamically generated test atmosphere.

5. References

5.1 Trade names Database on CCINFO CD-ROM Disc 95-2, Canadian Centre for Occupational Health and Safety, Hamilton, Ontario.

5.2 Lide, D. R., "Handbook of Chemistry and Physics," 73rd Edition, CRC Press Inc., Boca Raton FL, 1992, p. 3-29.

5.3 Windholz, M., "The Merck Index," Eleventh Edition, Merck & Co., Rahway NJ, 1989, p. 154.