



p-Chloroaniline

Method number: PV2109

Target concentration: 5 ppm (No PEL or TLV)

Procedure: Samples are collected by drawing a known volume of air through a silica gel tube. Samples are desorbed with methanol and analyzed by liquid chromatography with an ultraviolet detector at 254 nm (LC-UV).

Air volume and sampling rate studied: 60 minutes at 0.1 liters/minute (6 L)

Status of method: Partially Validated method. This method has been only partially evaluated and is presented for information and trial use.

September, 1986

Mary E. Eide

Solvent Branch
OSHA Salt Lake Technical Center
Sandy, UT-84070

1 General Discussion

1.1 Background

1.1.1 History of procedure

The OSHA Laboratory recently received samples collected on silica gel requesting analysis for p-chloroaniline. Several analytical procedures were tried, including gas chromatography and liquid chromatography, but the sensitivity of the liquid chromatography method was greater, and therefore it was used. The liquid chromatograph had an ultraviolet detector set at 254 nm; a secondary wavelength of 280 nm can also be used. The samples were desorbed with methanol and the desorption efficiency was 100%.

1.1.2 Potential workplace exposure

Workers are exposed to p-chloroaniline in many industries, with the majority of them in the chemical manufacturing industries. It is used in azoic coupling compounds and dye manufacturing (Ref. 5.1).

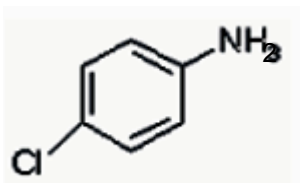
1.1.3 Toxic Effects (This section is included for information only and should not be taken as the basis of OSHA policy.)

Exposure to p-chloroaniline is irritating to skin, eyes, mucous membranes, and through oral ingestion and inhalation. Upon entering the bloodstream, p-chloroaniline damages the blood cells. The lowest toxic concentration by inhalation in humans was 44 mg/m³ (8.4 ppm). The lowest lethal dose (LD₅₀) through oral ingestion in rats was 300 mg/kg. The lowest lethal dose (LD₅₀) applied dermally in rabbits was 36 mg/kg (Ref. 5.2).

1.1.4 Physical properties: (Ref. 5.3)

Molecular weight:	127.57
Melting point:	72.5 °C
Boiling point:	232 °C
Odor:	aniline-like
Color:	white to pale gray
Vapor pressure:	1 mm at 59.3 °C
Molecular formula:	C ₆ H ₄ NH ₂

Structure:



1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 6 ng/injection. This is the smallest amount that could be easily detected under normal analytical conditions. The injection size was 10 µL.

1.2.2 The detection limit of the overall procedure is 6 ng/sample (0.02 ppm based on a 6-liter sample). This is the amount of analyte placed on a silica gel tube which corresponds to the detection limit of the analytical procedure.

1.3 Advantages

- 1.3.1 The sampling procedure is convenient.
- 1.3.2 The analytical method is reproducible and sensitive.
- 1.3.3 Re-analysis of samples is possible.
- 1.3.4 It may be possible to analyze other compounds at the same time.
- 1.3.5 Interferences may be avoided by proper selection of column and parameters.

1.4 Disadvantages

- 1.4.1 Silica gel tubes adsorb water vapor from the air; thereby, possibly lowering the capacity of the tube for p-chloroaniline.

2 Sampling procedure

2.1 Apparatus

- 2.1.1 A calibrated personal sampling pump, the flow of which can be determined within $\pm 5\%$ at the recommended flow.
- 2.1.2 Silica gel tubes (20/40 mesh) containing 150-mg adsorbing section with a 75-mg backup section separated by a 2 mm portion of urethane foam, with a silane-treated glass wool plug before the adsorbing section and a 3-mm plug of urethane foam at the back of the backup section. The ends are flame sealed and the glass tube containing the adsorbent is 7-cm x 6-mm o.d. and 4-mm i.d., SKC tubes or equivalent.

2.2 Sampling technique

- 2.2.1 The ends of the silica gel tube are opened immediately before sampling.
- 2.2.2 Connect the silica gel tube to the sampling pump with flexible tubing.
- 2.2.3 Tubes should be placed in a vertical position to minimize channeling, with the smaller section towards the pump.
- 2.2.4 Air being sampled should not pass through any hose or tubing before entering the silica gel tube.
- 2.2.5 Seal the silica gel tube with plastic caps immediately after sampling. Seal each sample lengthwise with a Form OSHA-21 seal.
- 2.2.6 With each batch of samples, submit at least one blank tube from the same lot used for samples. This tube should be subjected to exactly the same handling as the samples (break ends, seal, & transport) except that no air is drawn through it.
- 2.2.7 Transport the samples (and corresponding paperwork) to the lab for analysis.
- 2.2.8 Bults submitted for analysis must be shipped in a separate container from the samples.

2.3 Desorption efficiency

2.3.1 The desorption efficiency averaged 101% at the concentration of 149.2 µg loading on the tubes, or 4.77 ppm based on a 6 liter air sample (see Table 2.3.2).

2.3.2 The desorption study was generated by spiking 298.3, 149.2, or 74.59 µg of p-chloroaniline onto six tubes at each level and storing overnight at room temperature. They were opened the next day, desorbed with 1-mL methanol, and analyzed by LC-UV.

Table 2.3.2

level spiked (µg)	% recovered	level spiked (µg)	% recovered	level spiked (µg)	% recovered
74.59	99.1	149.2	101	298.3	98.7
74.59	98.4	149.2	101	298.3	102
74.59	101	149.2	99.8	298.3	102
74.59	101	149.2	102	298.3	102
74.59	102	149.2	101	298.3	99.7
74.59	104	149.2	102	298.3	99.8
average	101	average	101	average	101

overall average = 101
standard deviation = ±1.4

2.4 Retention efficiency

2.4.1 The retention efficiency was performed by liquid spiking 149.2 µg p-chloroaniline on silica gel tubes and drawing a known volume of humid air (R.H. 86%) through the tubes. There was little loss of the p-chloroaniline (see Table 2.4.2).

2.4.2 Twelve samples were spiked with 149.2 µg p-chloroaniline. Six had 3 liters, and the other six samples had 6 liters of humid air drawn through them. There was 1.6% loss with 3 liters and 2.9% loss with 6 liters humid air drawn.

Table 2.4.2

tube #	liters drawn	% recovered	tube #	liters drawn	% recovered
1	3	98.0	7	6	98.2
2	3	98.8	8	6	96.0
3	3	99.7	9	6	98.2
4	3	99.3	10	6	98.1
5	3	96.4	11	6	95.0
6	3	96.4	12	6	lost
average	3	98.4	average	6	97.1

2.5 Storage

2.5.1 Storage study was performed over a 14-day period with little loss of p-chloroaniline (see Table 2.5.2).

2.5.2 The tubes were spiked with 149.2 µg/tube with p-chloroaniline. They were analyzed on days 1, 6, 11, and 14. The day 1 samples were used for the desorption study.

Table 2.5.2

day	% recovered	average
1	101	
1	101	
1	99.8	101%
1	102	
1	101	
1	102	
6	96.5	
6	97.3	96.5%
6	95.6	
11	99.6	
11	97.9	99.1%
11	99.8	
14	97.5	
14	97.3	98.3
14	100	
overall average =98.7%		

2.6 Air volume and sampling rate studied

2.6.1 The air volume studied was 6 liters.

2.6.2 The sampling rate studied was 0.1 liters per minute.

2.7 Interferences

2.7.1 Water vapor may cause a decrease in the collection capacity of p-chloroaniline.

2.7.2 Suspected interferences should be listed on sample data sheets.

2.8 Safety precautions

2.8.1 Sampling equipment should be placed on an employee in a manner that does not interfere with work performance or safety.

2.8.2 Safety glasses should be worn at all times.

2.8.3 Follow all safety practices that apply to the workplace being sampled.

3 Analytical method

3.1 Apparatus

3.1.1 Liquid chromatograph equipped with an ultraviolet detector at 254 nm.

3.1.2 LC column capable of separating the analyte from any interference. An Alltech C18 column was used in this evaluation.

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

3.1.4 Two milliliter vials with PTFE-lined caps.

- 3.1.5 A 10- μ L syringe or other convenient size for sample injection.
- 3.1.6 Pipettes for dispensing the desorbing solvent. The Glenco 1-mL dispenser was used in this method.
- 3.1.7 Volumetric flasks, 10 mL, and other convenient sizes for preparing standards.

3.2 Reagents

- 3.2.1 Methanol HPLC grade.
- 3.2.2 Millipore deionized water.

3.3 Sample preparation

- 3.3.1 Sample tubes are opened and the front and back section of each tube are placed in separate 2-mL vials.
- 3.3.2 Each section is desorbed with 1 mL methanol.
- 3.3.3 The vials were sealed immediately and allowed to desorb for 30 minutes with occasional shaking.

3.4 Standard preparation

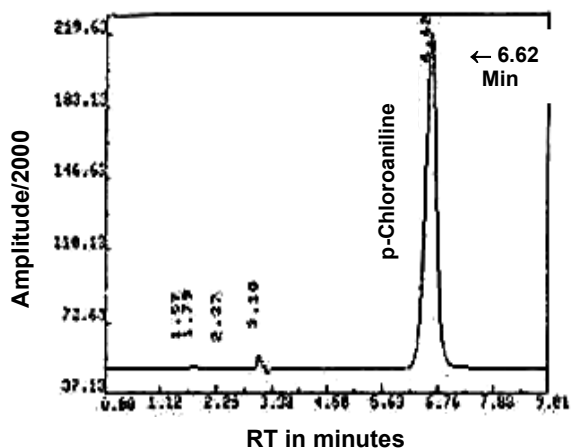
- 3.4.1 Standards were prepared by diluting a known quantity of p-chloroaniline with methanol.
- 3.4.2 At least two separate stock standards should be made. Dilutions of these stock standards are made. The range used in this method was from 1492 μ g/mL to 0.6 μ g/mL.

3.5 Analysis

3.5.1 Liquid chromatograph conditions

Solvent mixture: (65/35) methanol/water
Injection size: 10 μ L
Elution time: 6.62 minutes
Wavelength: 254 nm
Flow rate: 1mL/min
Column: Alltech C18

Chromatogram:



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

3.6 Interferences (analytical)

3.6.1 Any compound having the general retention time of the analyte is interference. Possible interferences should be listed on the sample data sheet. LC parameters should be adjusted, if necessary, so these interferences will pose no problems.

3.6.2 Retention time data on a single column is not considered proof of chemical identity. Samples over the target concentration should be confirmed by GC/Mass Spec or other suitable means.

3.7 Calculations

3.7.1 The following equation was used to calculate the ppm of analyte in standards based on a 6-liter air sample, and a 1-mL desorbing solution:

$$mg / m^3 = \frac{(\mu g / mL)(DV)}{(L)(DE)}$$

$\mu g/mL$ = Concentration of analyte in sample or standard

DV = Desorption volume

L = air sample collected

DE = Desorption efficiency

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

3.8 Safety precautions

3.8.1 All handling of solvents should be done in a hood.

3.8.2 Avoid skin contact with all solvents.

3.8.3 Wear safety glasses at all times.

4 Recommendations for further study include vapor-generated samples in both dry and humid air to check adsorption of p-chloroaniline on silica gel tubes. Since there may be a problem with water vapor replacing the p-chloroaniline on the silica gel tubes, the retention efficiency at larger air volumes of humid air needs to be studied. Other studies as needed to complete method validation.

5 References

5.1 Mark, H.F., Othmer, DF, Overberger, C.G., Seaborg, G.T., "Encyclopedia of Chemical Technology," Third Edition, John Wiley & Son, N.Y., 1978, Vol. 2, p. 318.

5.2 Sax, N.I., "Dangerous Properties of Industrial materials," Fifth Edition, Van Nostrand Reinhold Co., N.Y., 1979, p.488.

5.3 Windholz, M., "The Merck Index," Tenth Edition, Merck & Co., Rahway N.J., 1983, p.297.