

# The Determination of Metals in Chlorinated Hydrocarbons by Flame Atomic Absorption

## Application Note

Atomic Absorption

### Author

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### Introduction

A demand for the determination of metals in chlorinated hydrocarbons has increased in recent months. Metal contamination can originate with the raw materials and from contact with process equipment during manufacture. The metals content must be closely monitored in the final product.

The analysis of chlorinated hydrocarbons presents problems in flame atomic absorption spectroscopy (FAAS). Chlorinated hydrocarbons break down into toxic organic compounds with flame combustion. McKenzie [1] recommends against aspirating chlorinated hydrocarbons into the flame because of the formation of phosgene. Therefore, an alternate method of analysis is necessary.

This paper presents an alternate method of determining metals in chlorinated hydrocarbons. The chlorinated hydrocarbons are evaporated under safe laboratory conditions. The metal containing residue is dissolved in a solvent suitable for direct flame aspiration. In this study, two solvents were investigated initially, 2% hydrochloric acid (2% HCl) and methyl isobutyl ketone (MIBK).



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## Procedure

The chlorinated hydrocarbon samples were slowly evaporated using a heat lamp and fume hood. A laboratory hot plate could be substituted for the heat lamp. Sychra [2] reported a similar procedure for the analysis of metals in various short-chained organic solvents. Another similar method is the evolution of 1, 1, 2-trichloro-1, 2, 2-trifluoroethane (Freon 113) in the oil and grease partition-gravimetric method used by the American Public Health Association [3].

Blank, standard and sample aliquots of 100 mL were carefully evaporated to dryness. The remaining residue was then dissolved in a few mL of 2% HCl or MIBK. The blank, standards and samples were then diluted to 100 mL. The analyst may use different final volumes to concentrate the samples when determining trace levels. The prepared samples were used to determine percent recoveries and thus the viability of the method. The chlorinated hydrocarbons investigated, with their respective boiling points, are listed in Table 1.

Table 1. Chlorinated Hydrocarbons Investigated

Name	B. P. °C
Chloroform	61.2
1, 1, 1-Trichloroethane	74.0 – 76.0
+1, 1, 2-Trichloro-1, 2, 2-trifluoroethane*	50.0

\*Freon 113

The boiling points help the analyst determine how fast the chlorinated hydrocarbons can be evaporated. The analyst should take care not to drive off any of the more volatile metals.

Three metals, aluminium, iron and nickel were studied. Standards were prepared from organic salts of the metals. The salts must be soluble in the chlorinated hydrocarbon or solvent under investigation as discussed by Sychra [2]. Aluminium, iron (III) and nickel 2, 4-pentanedionate salts were chosen. Standards of 1000 mg/L in acetone were prepared. The standards were then diluted with the three chlorinated hydrocarbons to give the concentrations shown in Table 2.

Table 2. Concentration of Prepared Standards

Metal	Standard 1 mg/L	Standard 2 mg/L	Standard 3 mg/L
Aluminium	10.0	30.0	50.0
Iron	1.0	2.5	5.0
Nickel	1.0	2.5	5.0

1, 3 and 5 mL of 1000 mg/L aluminium and 100, 250 and 500 µL of 1000 mg/L iron and nickel were added to the chlorinated hydrocarbons and brought to a final volume of 100 mL to prepare the working standards.

The sample concentrations were 40 mg/L aluminium, 2.0 mg/L iron and 3.0 mg/L nickel. They were prepared by adding 4 mL aluminium, 200 µL iron and 300 µL nickel (1000 mg/L) to 100 mL of the chlorinated hydrocarbons. Following evaporation of the chlorinated hydrocarbons, the blank, standards and sample residues were dissolved. A few mL of 2% HCl or MIBK were added to the respective evaporation beakers. The 2% HCl was heated and stirred for 30-45 minutes. The MIBK was stirred for 30-45 minutes. The solutions were quantitatively transferred to 100 mL volumetric flasks and brought to volume with successive rinsing of the beakers.

## Instrumentation

The instrumentation employed was the Agilent AA-975 Atomic Absorption Spectrometer and Hewlett-Packard 86A computer. The parameters for the aqueous (2% HCl) solutions are shown in Figure 1. Figure 2 gives the parameters for the MIBK solutions. For MIBK, the glass bead was adjusted to give maximum sensitivity with standards and the nebulizer uptake rate was reduced to 1.4 mL/min. McKenzie [4] states that these adjustments are necessary when conducting analyses with organic solvents. As shown in Figure 2, the air:acetylene ratio was increased to compensate for the excess fuel added by the organic solvent.

AA-975		AA-975		AA-975	
PROGRAM ID	2.	PROGRAM ID	6.	PROGRAM ID	7.
INT TIME	5.0	INT TIME	5.0	INT TIME	5.0
WAVELENGTH	248.3	WAVELENGTH	232.2	WAVELENGTH	309.3
SLIT	0.2	SLIT	0.2	SLIT	0.5
LAMP NUMBER	2.	LAMP NUMBER	6.	LAMP NUMBER	7.
LAMP CURRENT	5.	LAMP CURRENT	4.	LAMP CURRENT	10.
EXPN FACTOR	1.	EXPN FACTOR	1.	EXPN FACTOR	1.
STANDARD 1	0.	STANDARD 1	0.	STANDARD 1	0.
STANDARD 2	0.	STANDARD 2	0.	STANDARD 2	0.
STANDARD 3	0.	STANDARD 3	0.	STANDARD 3	0.
ABS		ABS		ABS	
BC OFF		BC OFF		BC OFF	
INT HOLD		INT HOLD		INT HOLD	
AIR SET UP	13.0	AIR SET UP	13.0	N2O SET UP	11.0
ACET SET UP	2.00	ACET SET UP	2.00	ACET SET UP	5.00

Figure 1.

AA-975		AA-975		AA-975	
PROGRAM ID	2.	PROGRAM ID	6.	PROGRAM ID	7.
INT TIME	5.0	INT TIME	5.0	INT TIME	5.0
WAVELENGTH	248.3	WAVELENGTH	232.2	WAVELENGTH	309.3
SLIT	0.2	SLIT	0.2	SLIT	0.5
LAMP NUMBER	2.	LAMP NUMBER	6.	LAMP NUMBER	7.
LAMP CURRENT	5.	LAMP CURRENT	4.	LAMP CURRENT	10.
EXPN FACTOR	1.	EXPN FACTOR	1.	EXPN FACTOR	1.
STANDARD 1	0.	STANDARD 1	0.	STANDARD 1	0.
STANDARD 2	0.	STANDARD 2	0.	STANDARD 2	0.
STANDARD 3	0.	STANDARD 3	0.	STANDARD 3	0.
ABS		ABS		ABS	
BC OFF		BC OFF		BC OFF	
INT HOLD		INT HOLD		INT HOLD	
AIR SET UP	13.6	AIR SET UP	13.5	N2O SET UP	12.0
ACET SET UP	1.42	ACET SET UP	1.87	ACET SET UP	6.47

Figure 2.

## Results

The results for the two solvents used are summarized in Table 3. The results reported in the table are blank corrected.

Table 3. Results (mg/L)

	Aluminium		Iron		Nickel	
	Acid	MIBK	Acid	MIBK	Acid	MIBK
Freon 113	37.51	48.36	1.97	2.10	2.34	1.12
Trichloroethane	36.80	38.78	1.95	2.03	2.43	5.00
Chloroform	37.86	31.92	1.88	1.79	2.54	0.75
Actual	40.00	40.00	2.00	2.00	3.00	3.00

As stated previously, the added concentrations were 40 mg/L aluminium, 2.0 mg/L iron and 3.0 mg/L nickel. Results for 2% HCl and MIBK differed and will be discussed separately.

## MIBK

Table 4 shows the per cent recovery of the three metals in the different chlorinated hydrocarbons.

Table 4. Per Cent Recovery of Metals, MIBK Solvent

	Aluminium	Iron	Nickel
Freon 113	120.9%	105.0%	37.6%
Trichloroethane	96.9%	101.5%	166.7%
Chloroform	79.8%	89.5%	25.5%

The recoveries obtained using MIBK to dissolve the metals from evaporated chlorinated hydrocarbons were poor. The MIBK dissolved the residual organic material but did not quantitatively bring the metals back into solution. Precisions for the determination of the metals varied when MIBK was used. The precision ranges (%RSD) were as follows:

Aluminium	0.0 to 0.9 %RSD
Iron	0.0 to 0.8 %RSD
Nickel	4.1 to 25.0 %RSD

The use of MIBK to dissolve the metallic residue was not considered viable.

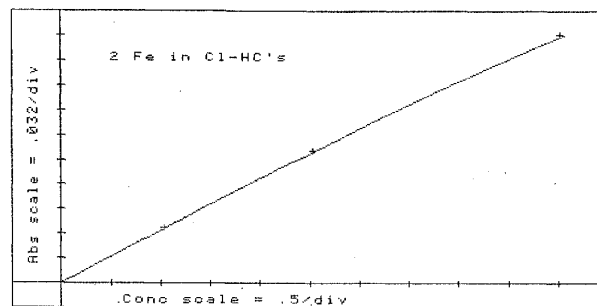
## 2% HCl

When 2% HCl was used, recoveries generally improved. The acid dissolved both the organic and the metallic residue. The metals dissolved more uniformly, producing more consistent results for the three metals in the different chlorinated hydrocarbons. It should be noted at this point that the standards were not carried through the evolution process. They were mixed standards prepared in 2% HCl. The blank and sample residues were dissolved in 2% HCl. The results were good as shown in Figures 3 and 4 (iron and aluminium calibrations respectively).

### VARIAN AA-975

OPERATOR: Deen Johnson  
DATE: 17 November 1983  
BATCH: Chlorinated Hydrocarbons (Acid)

AUTO-PROGRAM 2 SOLUTION	Fe in Cl-HC's CONC mg/L	RSD	MEAN ABS	ABSORBANCE READINGS							
BLANK	0.000	0.0%	0.001	0.001	0.001	0.002	0.002	0.002	0.002	0.002	0.002
STANDARD 1	1.000	0.0%	0.068	0.068	0.069	0.068	0.067	0.068	0.068	0.068	0.068
STANDARD 2	2.500	0.6%	0.168	0.170	0.170	0.167	0.167	0.167	0.167	0.167	0.167
STANDARD 3	5.000	0.6%	0.316	0.317	0.317	0.318	0.319	0.319	0.319	0.319	0.319



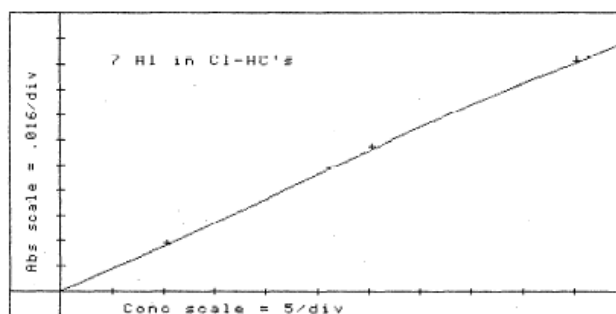
Freon	1.980	0.7%	0.134	0.136	0.136	0.134	0.134	0.134	0.134	0.134	0.134
Freon/B	0.014	100.0%	0.001	0.001	0.003	0.002	0.001	0.001	0.001	0.001	0.001
TCE	2.041	0.7%	0.138	0.140	0.138	0.140	0.139	0.137	0.137	0.137	0.137
TCE/B	0.088	16.7%	0.006	0.007	0.005	0.007	0.008	0.006	0.006	0.006	0.006
CF	1.950	0.8%	0.132	0.131	0.134	0.135	0.132	0.132	0.132	0.132	0.132
CF/B	0.073	20.0%	0.005	0.005	0.007	0.005	0.006	0.006	0.006	0.006	0.006

Figure 3.

### VARIAN AA-975

OPERATOR: Deen Johnson  
DATE: 17 November 1983  
BATCH: Chlorinated Hydrocarbons (Acid)

AUTO-PROGRAM 7 SOLUTION	Al in Cl-HC's CONC mg/L	RSD	MEAN ABS	ABSORBANCE READINGS							
BLANK	0.000	0.0%	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
STANDARD 1	10.00	3.6%	0.028	0.028	0.028	0.026	0.030	0.029	0.029	0.029	0.029
STANDARD 2	30.00	1.1%	0.089	0.090	0.090	0.090	0.088	0.089	0.089	0.089	0.089
STANDARD 3	50.00	0.7%	0.144	0.145	0.143	0.145	0.144	0.146	0.146	0.146	0.146



Freon	37.51	0.0%	0.111	0.111	0.111	0.112	0.110	0.111	0.111	0.111	0.111
Freon/B	0.000	0.0%	0.000	0.001	0.000	0.001	0.001	0.001	0.001	0.001	0.001
TCE	37.16	0.9%	0.110	0.112	0.111	0.111	0.110	0.109	0.109	0.109	0.109
TCE/B	0.357	100.0%	0.001	0.002	0.001	0.002	0.002	0.002	0.002	0.002	0.002
CF	37.86	3.6%	0.112	0.114	0.112	0.108	0.109	0.118	0.118	0.118	0.118
CF/B	0.000	0.0%	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Figure 4.

The recovery of the metals using 2% HCl to dissolve the residue is shown in Table 5.

Table 5. Per Cent Recovery of Metals, 2% HCl Solvent

	Aluminium	Iron	Nickel
Freon 113	93.8%	98.5%	78.0%
Trichloroethane	92.0%	97.5%	81.0%
Chloroform	94.7%	94.0%	84.7%

Aluminium and iron in the three chlorinated hydrocarbons showed good recovery percentages, better than 92.0%. The nickel recovery was not as good (78.0 to 84.7%) but was much more consistent and precise than recoveries reported for MIBK. The precisions using 2% HCl were good for all three metals from the different solvents. Precisions were as follows:

Aluminium	0.0 to 3.6 %RSD
Iron	0.7 to 0.8 %RSD
Nickel	1.8 to 2.6 %RSD

Further study was done in an attempt to improve the recovery of the nickel. Three additional solvents were investigated in an attempt to recover at least 99.0% of the nickel. The solvents were concentrated hydrochloric acid (HCl), 5% hydrochloric acid (5% HCl) and 5% nitric acid (5% HNO<sub>3</sub>).

When concentrated hydrochloric acid was used, 5 mL was added to the evaporation beaker. The acid and dissolved residue was transferred to a 100 mL volumetric flask and brought to volume. All three concentrations were heated and stirred for 30–45 minutes before quantitative transfer.

The results for the three chlorinated hydrocarbons are shown in Table 6. Again these results are blank corrected. It should be noted that there was not enough Freon 113 sample to carry through the tests with all three additional solvents.

Table 6. Nickel Results (mg/L)

	HCl 5%	HCl 5%	HNO <sub>3</sub>
Freon	—	2.50	—
Trichloroethane	2.98	3.21	3.05
Chloroform	2.77	2.72	2.85
Actual	3.00	3.00	3.00

The recovery of nickel using these additional solvents is reported in Table 7.

Table 7. Per Cent Recovery of Nickel

	HCl 5%	HCl 5%	HNO <sub>3</sub>
Freon	—	83.5%	—
Trichloroethane	99.3%	107.0%	101.8%
Chloroform	92.3%	90.9%	94.9%

The precision for the additional analyses ranged from 0.6 to 2.5 %RSD.

The acid tests improved the nickel recovery to better than 90.0% in all but the Freon 113 analysis. The concentrated HCl and HNO<sub>3</sub> gave the best and most consistent recoveries (92.3 to 101.8%). The 5% HCl did not give consistent recoveries for the nickel and was in fact poorer than 2% HCl.

## Conclusions

The method described is viable for determining metals content in chlorinated hydrocarbons safely. The use of acid to dissolve the residue after evaporation of the chlorinated hydrocarbons showed good recoveries for the metals studied. The results show that the analyst can expect good to excellent accuracy and precision with the method.

For best results, it is imperative that the analyst make recovery determinations. The recoveries vary for different metals, for different chlorinated hydrocarbons and different solvents used to dissolve the evaporation residues.

The use of MIBK to dissolve the evaporation residue is not recommended. Recoveries are extremely variable and the accuracy and precision is poorer than that obtained when acid is used.

Better results may be possible if the blank, standards and samples are all carried through the evolution process, rather than preparing a mixed standard in dilute acid.

The method may also be useful for the determination of metals in other organic solvents. Samples that have potential problems with safety, poor burning characteristics or sample handling problems should be considered for the evaporation technique.

## References

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