

ANALYSIS OF WATER FOR PPB RANGE CHLORINATED ORGANICS USING A TOTAL ORGANIC CHLORINE ANALYZER

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ABSTRACT

Dexsil Corporation has recently developed a total halogen method for the analysis of water samples for chlorinated organics. The new procedure is an addition to the existing methods for the L2000DX Chloride Analyzer. The L2000DX has been in use in the field for 12 years and can be used for the analysis of transformer oil, surface wipes and soils. The soil method is the basis for SW-846 Method 9078 "Screening Test Method for Polychlorinated Biphenyls in Soil." Using the same reaction and quantification steps as the established L2000DX methods, the new method uses a liquid-liquid extraction step to achieve method detection limits (MDLs) in the 15-30 ppb range for most chlorinated solvents. This new method will allow nearly real time data to be collected from ground water monitoring wells at a fraction of the cost of laboratory analysis.

This paper describes the new method, the development work in establishing the feasibility of the method and the comparison with SW-846 laboratory methods for spiked samples. Recoveries and MDLs have been determined for the following analytes: Carbon Tetrachloride, 1,2-Dichloroethane (DCEA), cis-1,2-Dichloroethylene (DCEE), trans-1,2-Dichloroethylene (DCEE), 1,2-Dichloroethylene (cis/trans mix), Methylene Chloride, Pentachlorophenol (PCP), Tetrachloroethylene (PCE), 1,1,1-Trichloroethane (TCEA), Trichloroethylene (TCEE), Vinyl Chloride. As expected, the extraction recoveries vary inversely with the solubility of the analyte in water which, in turn, affects the MDL for the analyte. The MDLs for these analytes range from 16 ppb for carbon tetrachloride to 157 ppb for methylene chloride with the majority around 25 ppb.

The method development data indicate that the L2000DX water method should be a useful tool for monitoring ground water in areas contaminated with chlorinated solvents. Now, one instrument can be used to track contamination in both soil and water. This type of screening can be used for checking the progress of a treatment process, defining the limits of a contamination plume, as well as, monitoring ground water over long periods of time. All of these applications do not require expensive laboratory analysis and the L2000DX can provide the information in the field in 10 minutes.

INTRODUCTION

The L2000DX is a screening tool for chlorinated organic compounds and has been used in the field for the analysis of transformer oil for PCB contamination since 1989. Shortly after its introduction, a method was developed to use the L2000DX for the screening of soils for PCBs. This method eventually became SW-846 Method 9078¹ and has been evaluated in two different forms, first, through the SITE program and, most recently, under the ETV program² both run by the USEPA. The procedure for PCBs in transformer oil has just recently been validated through the ETV program and a method has also been developed for use on wipe samples.³

In the late 90s, with the rise of chlorinated solvents and pesticides as contaminants in the environment, the demand grew for the development of L2000DX based methods for other chlorinated compounds in soil. Laboratory experiments and field trials have since demonstrated that the L2000DX, following suitable matrix preparation, is suited to the analysis of basically any extractable chlorinated organic in soil.⁴

As chlorinated solvents leach into ground water and interest in cleaning up old dry cleaning and manufacturing sites grows, so has the need for an L2000DX method for water analysis. The objective of this work was to develop and document a water extraction technique for concentrating organo-chlorine contaminants into an organic solvent suitable for introduction into the L2000DX system.

The L2000DX is a total chlorine analyzer. A requirement for the system is that all chlorine must be chemically converted to inorganic chloride for quantification. By changing the sample preparation steps either total chlorine or total organic chlorine will be measured. There are three elements to the analysis: sample preparation/extraction, converting the organic chlorine present into inorganic chloride using metallic sodium and the quantification of the resulting chloride using a chloride ion selective electrode (ISE). Over the 12 years of its use in the field, the L2000DX has proven to be a very reliable instrument and the ISE based system has been shown to be accurate and relatively free of interferences. (NOTE: All organic chlorine is quantified as the target analyte, however, this is the nature of a TOC measurement and is not an interference, per se. Inorganic chloride can be an interference, but can be removed in the matrix cleanup step and, therefore, would not interfere.)

There are four basic corrections necessary to convert the final chloride reading into the equivalent analyte concentration in the desired units. Three of the corrections are derived corrections calculated from the known chlorine composition of the analyte (percent chlorine), the dilution/extraction volumes of the matrix preparation steps and the conversion to the appropriate units. The fourth correction necessary to obtain a useful result is derived from empirical data on the overall efficiency of the analytical steps, including the extraction efficiency from the original matrix, the reaction efficiency for the conversion to chloride, the recovery of the chloride ions in the final buffer solution, etc. The theoretical conversion factors can be calculated for all analytes and tabulated for each matrix, but the correction for recoveries must be experimentally determined for each matrix and each analyte.

After some experimentation, it was determined that a simple liquid/liquid extraction would be the simplest and also effective. Of the commonly used solvents, e.g., hexane, heptane, cyclohexane, it was determined that 2,2,4-trimethylpentane (isooctane) worked well and had the advantage of being less volatile. A liquid/liquid extraction will accomplish two things: by choosing the appropriate solvent, it eliminates interferences due to inorganic chloride and by choosing the correct solvent to sample ratio, a concentration of 1:100 can easily be accomplished.

The effectiveness of a liquid/liquid extraction is determined primarily by the extracted compound and is, therefore, not constant over all possible contaminants. In general, compounds with a high water solubility will tend to have low recoveries in the solvent layer. Extraction efficiency can also be affected by water quality parameters, e.g., pH, salinity, ionic strength, etc. In this work we set out to determine the extraction efficiency for a liquid/liquid extraction combined with the L2000DX sample preparation as well as the MDL for the quantification of environmentally significant organo-chlorine contaminants.

EXPERIMENTAL

All samples were prepared in 965 mL of deionized water, cooled overnight, in 1-quart glass jars from Quality Environmental Containers. The majority of the water samples were between 11 and 14 EC when extracted, determined after the extraction was complete. The temperature was varied between 2EC and 45EC for water samples used to determine the effects of temperature on the extraction of methylene chloride. To study the effects of ionic strength, pH and salinity on the recovery of methylene chloride, deionized water was first spiked with either 1% sodium sulfate, hydrochloric acid (pH < 2), sodium hydroxide (pH > 12) or 1% sodium chloride, shaken and then refrigerated. Recovery experiments using PCP were also conducted on pH adjusted water.

Each day, a fresh stock solution of approximately 2500 ppm of a single analyte was prepared in methanol. Appropriate volumes of stock solution were injected by syringe into the cooled water to yield the desired analyte concentrations. Each jar was gently turned to ensure mixing of the analyte, while minimizing its partitioning into the headspace. To determine the method recoveries and linearity, duplicate samples were prepared at the following concentrations: 0.15, 0.25, 0.50, 1.0, 2.0, 5.0, and 10.0 ppm. Additionally, the MDL was determined for each analyte according to 40 CFR Part 136.⁵ The seven replicate water samples for each analyte were prepared in the same way at concentrations within a factor of 3-5 of the estimated MDL (See Table 1).

For chloride analysis by L2000DX, the analyte of each sample was extracted into 10 mL isooctane, followed by vigorous shaking for two minutes. The sample jars were then filled to zero headspace with deionized water, and the isooctane was allowed to settle in the neck of the bottle for at least three minutes. After the isooctane extract had settled, 5 mL were transferred into an L2000DX reaction tube. The samples were further prepared according to the instructions provided with the L2000DX instruction manual.⁶ This preparation involved the complete isolation of chloride ions from the analyte.

The L2000DX instrument was calibrated with a standard 50 ppm chloride solution. Before the samples were tested, standard 10 ppm and 1000 ppm chloride solutions were checked. The chloride content of all samples were measured using the uncorrected L2000DX Chloride Method.

Initial preparation of samples for GC analysis was identical to that of the L2000DX samples. For the GC readings, however, the samples were injected into a purge-and-trap device after the chlorinated solvent had been gently mixed into the 965 mL of water. For analyte concentrations up to 2 ppm, 5 mL of sample were drawn into a syringe with a Luer-Lock connection without a needle. Into this solution, 5 mL of an internal standard was injected. The internal standard consisted of a 2000 mg/mL solution of 2-bromo-1-chloropropane and fluorobenzene in methanol. This combined solution with internal standard was injected into the purge-and-trap device. For 5 ppm and 10 ppm solutions, 1 mL of sample was diluted to 5 mL with deionized water, then injected into the purge-and-trap along with 5 mL internal standard. The purge-and-trap served to extract all the low-boiling solvents out of the sample into the gas phase by bubbling an inert purge gas through the water. The analyte and internal standards were collected in the trap. After the purging was complete, all analytes that had collected into the trap were desorbed onto the GC column. A calibration curve of the analytes studied was made from 0.15 ppm to 2.0 ppm. The calibration curve and all samples were run using the EPA Volatiles 502.2 method.

PERC was additionally analyzed by GCMS, using EPA VOC Method 8260. The GCMS samples were also injected via purge-and-trap and most were diluted by a factor of 10 or 100, depending on the initial concentration of the samples. This method used an internal standard mixture of pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d5, and 1,4-dichlorobenzene at a fixed concentration reading of 50.00 mg/L. In the internal standard mixture, the surrogate analytes present were dibromofluoromethane, toluene-d8, and 4-bromofluorobenzene at concentrations of approximately 100.0 mg/L. A calibration curve for PERC was made of concentrations ranging from 5 ppb to 200 ppb.

RESULTS AND DISCUSSION

The methylene chloride experiments indicate that varying water quality parameters have little effect on the recovery of chlorinated solvents. While this means that the recovery of methylene chloride cannot be easily improved, it also indicates that variations in ground water should not significantly affect recoveries in the field. As expected, pH did affect the recovery of PCP. The recovery improved from 54% to 60% when the pH was reduced from neutral to less than 2.

The one water parameter that did have an affect on recovery of chlorinated solvents was temperature. Spiking water of various temperatures at 1 ppm with PCE, resulted in recoveries ranging from 35% at 2EC to approximately 60-65% at 12EC. Above 12EC the recoveries remained more or less constant in the 60-70% range, up to the highest temperature tested at 45 EC.

In order to determine the recoveries, theoretical corrections were made to the instrumental readings to account for percent chloride (on L2000DX readings only) and dilution/concentration factors. While the GC experiments analyzed the VOC analyte concentrations directly, the L2000DX uses a chloride-specific electrode, which measures free chloride concentration. The L2000DX readings were converted from chloride concentrations to analyte concentrations by dividing the measurement by the percent chlorine in the analyte. The extraction of the analyte from water to isooctane produced a size multiplier for the L2000DX samples of $965/10 = 96.5$. Although there was no extraction involved in the GC samples, a size multiplier of 5 was used for the most concentrated samples since these samples were diluted by a factor of five. Similarly for GCMS samples, the dilution factor was the size multiplier. Once these theoretical corrections

had been made, a regression analysis of the corrected instrument response versus the theoretical concentration for each analyte indicates the linearity of the response. Table 1 shows the comparison of the coefficient of regression for both the L2000DX and the GC/GCMS response curves. Figure 1 showing the measured concentration versus the theoretical concentration for PCE, illustrates a typical response curve for both methods. The slopes of the regression line can be taken as the average percent recoveries for each analyte, as shown in Table 2.

A plot of the average recovery versus the analyte solubility in water for all analytes tested, indicates that the recovery is inversely proportional to an analyte's solubility (See Figure 2). Using published data, it can be seen in Figure 3 that a reasonable approximation of the recovery can also be made based on an analytes octanol/water partition coefficient.⁷

The ultimate sensitivity of the L2000DX method is determined by the sensitivity of the ISE. The practical limit for chloride detection, with some low-end corrections, is 1 ppm in the final extract solution used for quantification. Since all of the preparation steps are the same for each analyte, and the final extraction multiplier is determined by the extraction efficiency, the achievable MDL for each analyte will, therefore, be a function of the recovery. The results from the MDL determinations, listed in Table 2, confirm this general trend with the lowest MDL of 16 ppb achieved for carbon tetrachloride (58% recovery) and the highest of 157 ppb for methylene chloride (9% recovery).

SUMMARY

The results from the response range experiments indicate that the L2000DX liquid/liquid extraction method for water is has a linear range up to 10 ppm for all of the analytes tested. The coefficient of regression was greater than 0.96 for all analytes including methylene chloride, the hardest to extract. The recovery for each of the analytes has been demonstrated to be consistent and reproducible enough to make this method a suitable method for field use. Typical MDLs are in the 25 ppb range for most of the analytes of interest which should make the L2000DX water method a useful tool for monitoring ground water in areas contaminated with chlorinated solvents. Now, one instrument can be used to track contamination in both soil and water. This type of screening can be used for checking the progress of a treatment process, defining the limits of a contamination plume, as well as, monitoring ground water over long periods of time. All of these applications do not require expensive laboratory analysis and the L2000DX can provide the information in the field in 10 minutes.

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TABLE 1: Comparison of Recoveries and Regression Coefficients for GC and L2000DX Response Curves

Analyte	L2000DX R ²	L2000DX Recovery	GC/GCMS R ²	GC Recovery
Carbon Tetrachloride	0.974	0.58	xx	xx
1,2-Dichloroethane (DCEA)	0.992	0.18	0.991	0.95
cis-1,2-Dichloroethylene (DCEE)	0.987	0.26	xx	xx
trans-1,2-Dichloroethylene (DCEE)	0.987	0.41	xx	xx
1,2-Dichloroethylene (cis/trans mix)	0.990	0.26	0.990	1.15
Methylene Chloride	0.992	0.09	xx	xx
Pentachlorophenol (PCP)	0.996	0.54 (0.6@pH<2)	xx	xx
Tetrachloroethylene (PCE)	0.969	0.59	0.973/0.990	1.20/1.19
1,1,1-Trichloroethane (TCEA)	0.989	0.37	0.991	1.16
Trichloroethylene (TCEE)	0.965	0.41	0.996	1.14
Vinyl Chloride	0.990	0.11	xx	xx

TABLE 2: Physical Data and L2000DX MDLs and Recoveries

Analyte	H ₂ O Sol. (wt %)	Typical Log K _{ow}	Recovery	Spike Level (ppb)	MDL (ppb)
Carbon Tetrachloride	0.08	2.6 (2.2-3)	0.58	51	16
1,2-Dichloroethane (DCEA)	0.81	1.5 (1.4-1.8)	0.18	250	71
cis-1,2-Dichloroethylene (DCEE)	0.35	1.7 (1.5-1.9)	0.26	xx	xx
trans-1,2-Dichloroethylene (DCEE)	0.63	1.9 (1.5-2.1)	0.41	xx	xx
1,2-Dichloroethylene (cis/trans mix)	xx	xx	0.26	150	86
Methylene Chloride	1.32	1.2 (1-1.5)	0.09	377	157
Pentachlorophenol (PCP)	0.008	3 (1.3-5.9)	0.54 (0.6@pH<2)	72	37
Tetrachloroethylene (PCE)	0.015	2.7 (2.4-3.4)	0.59	53	22
1,1,1-Trichloroethane (TCEA)	0.13	2.5 (2-2.6)	0.37	58	25
Trichloroethylene (TCEE)	0.11	2.3 (2-3.3)	0.41	63	23
Vinyl Chloride	0.88	1 (0.6-1.4)	0.11	207	94

Figure 1: Recovery of PCE from Water (omitting 2 outliers)

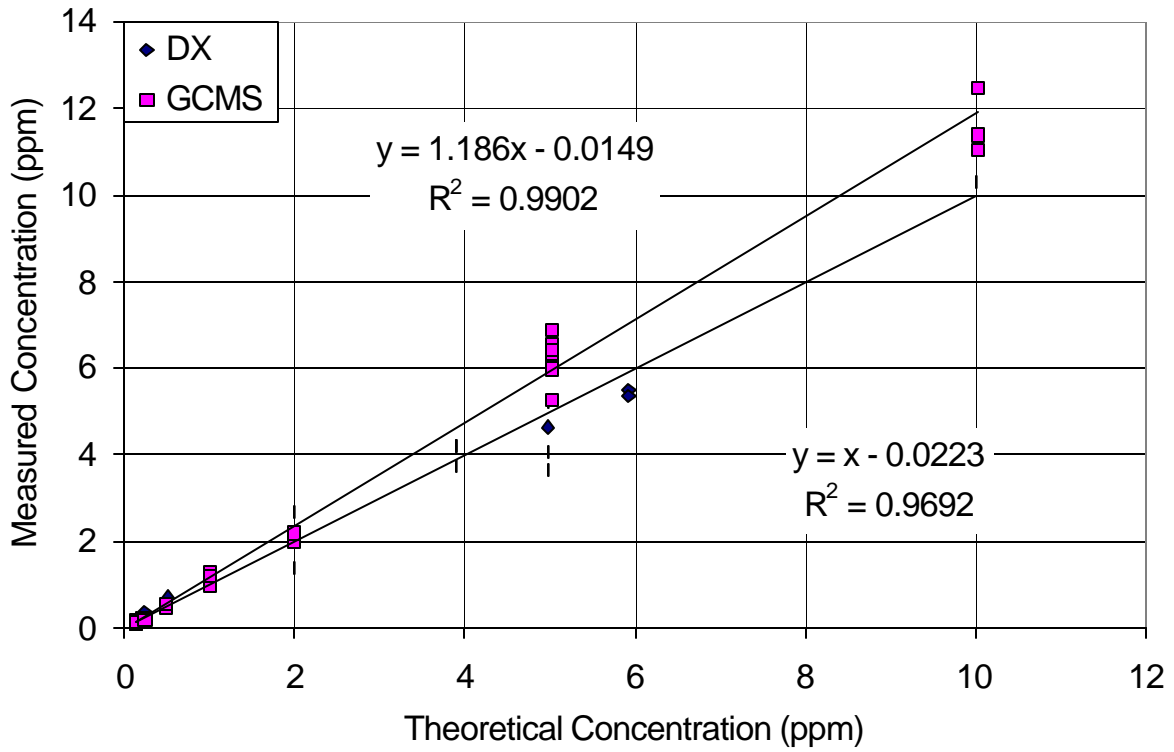


Figure 2: Recoveries Vs Solubilities (all analytes)

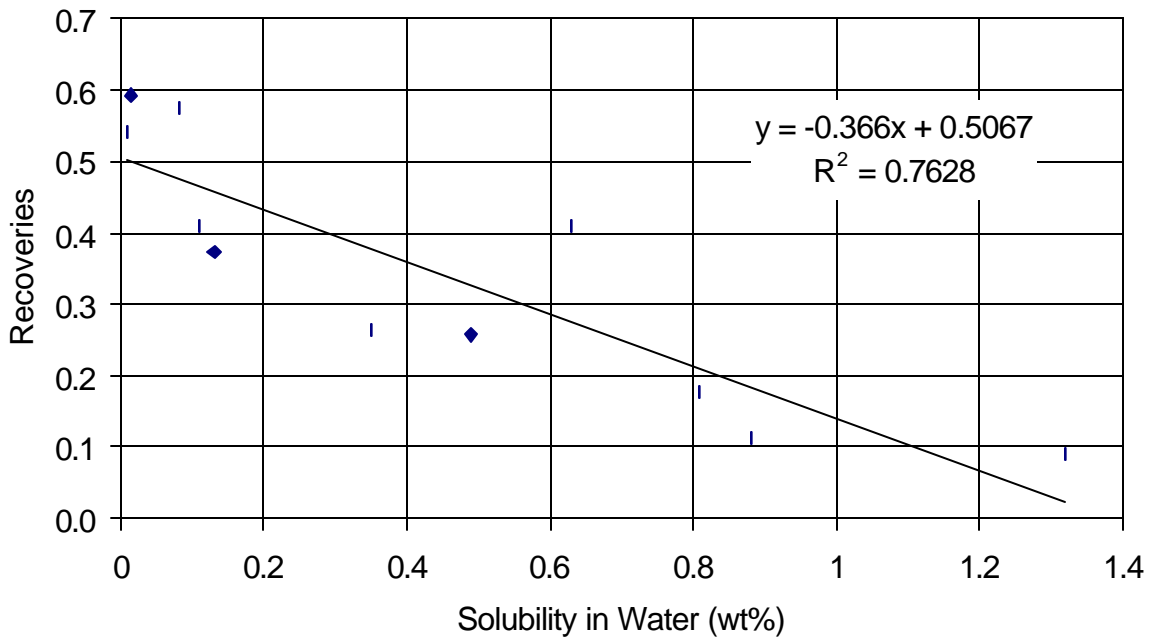


Figure 3: Recoveries Vs Log Kow (all analytes)

