



Project Summary

Direct Determination of Total Organic Chlorine in Water Without Preconcentration

Judith A. Gebhardt

The goal of this research effort was to develop instrumentation for the direct determination of total chlorinated organic compounds in aqueous samples without preconcentration. Two general approaches were investigated. The first involved isolation of the chlorinated organics from the sample matrix by flash evaporation. A catalytic conversion step was to produce free chlorine which was to be detected and quantified fluorometrically. This approach did not prove successful. An alternate procedure was investigated which used a piezoelectric crystal as the detection device. After evaluating a number of crystal coatings, Amine 220 was found to have appropriate characteristics. This material, a gas chromatographic stationary phase, has a high affinity for hydrochloric acid (HCl) and almost none for sodium chloride (NaCl), which is a major interference in total organic chloride (TOCl) or total organic halogen (TOX) determinations. In this procedure, the sample was delivered to the detector system by a direct injection of the aqueous sample through a quartz tube which is heated to approximately 600°C. Use of oxygen as the carrier gas created the oxidizing environment in which the chlorinated organics are converted to HCl.

The piezoelectric crystal coated with Amine 220 was found to have an absolute detection limit of approximately 100 pg of HCl. Assuming a minimum of 50 percent conversion efficiency, approximately three parts per billion (weight/volume) of chloroform should be detectable in a 100 μ L aqueous sample.

Difficulties were encountered in removing water from the system before it reached the detector system. Large amounts of water in contact with the Amine 220-coated piezoelectric crystal saturated the detector. Several modifications in the sample delivery system were investigated to remove the water. None were entirely successful, and additional work is necessary before the system is ready for further field evaluations.

This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Description of the Approaches

The first system investigated involved: (a) flash evaporation to separate chlorinated organics from salts; (b) oxidation of the chlorinated organics to free chlorine in a catalytic combustion furnace; (c) derivatization of the free chlorine with syringaldazine; and (d) fluorometric determination.

Two flash evaporators were evaluated in approach 1. The first was a simple horizontal, quartz tube operated at 400°C at pressures varying from atmospheric down to 100 millitorr. Flash evaporation of a 250 ppm solution of NaCl resulted in a high carryover of chloride ion. In an attempt to minimize chloride ion carryover, a second flask evaporator was designed incorporating a gravity separator and glass beads to facilitate the removal

of chloride vapor and particulate. This unit was evaluated at 400°C under ambient and subambient pressures using mixtures of Na³⁶Cl, ¹⁴CHCl₃, and ¹⁴C-PCB's. The experiment demonstrated that the subambient pressures required for good PCB recovery resulted in poor recovery for CHCl₃.

Ambient pressures resulted in good recoveries for CHCl₃ but poor recovery for PCB's. Under the conditions studied, the carryover ³⁶Cl was unacceptably high.

Syringaldazine reacts with hypochlorous acid to form a purple chromogen that absorbs in the visible region with a maxima at 530 nm. The detection limit using absorption maxima was too high to be useful for this application. Since the unoxidized reagent exhibits strong fluorescence at 530 nm at a pH of 8 or greater and at a wavelength at 420 nm at a pH of 4, it was anticipated that the oxidation product would also exhibit strong fluorescence properties. It was found that the oxidation product is unstable at a pH of less than 6 or greater than 8. After extracting and stabilizing the oxidation product, no evidence of fluorescence for the colored product was found.

The second system investigated involved: (a) introduction of the sample by direct injection; (b) conversion of the organochlorine compounds to HCl by non-catalytic oxidation; (c) removal of water from the reaction stream; and (d) detection of the HCl using a piezoelectric crystal coated with a reagent that preferably adsorbs acid halides.

The frequency at which a piezoelectric crystal oscillates is proportional to its mass. A piezoelectric crystal detector was assembled where the flow from the combustion/absorber train flowed across two piezoelectric crystals with nominal frequencies of 9.0 MHz. One crystal was coated with a chemical reagent that reversibly sorbs HCl while the other remained uncoated. A differential frequency counter monitored the changing frequency between the two crystals resulting in a signal proportional to the increased mass of the coated crystal as HCl was sorbed.

Ten different crystal coatings were evaluated in order to determine which coating is best suited for detecting HCl. The test was conducted by introducing 1-mL injections of reagent water and reagent water containing 500 ppm of HCl into a heated flask containing sulfuric acid. The resulting volatilized anhydrous HCl was swept into the detector by a nitrogen carrier gas. Table 1 presents the

response of the crystal for each coating evaluated compared to the response to the same volume of reagent water.

Quadrol, 4-aminoacetanilide, triethylenetetramine, and L-ornithine showed little or no response to HCl. The response of triphenylamine and triethanolamine were irreversible; that is, HCl was adsorbed but not released. After five replicate injections, the crystal coated with trimethylamine-HCl showed no further response. The substrate had become either degraded or saturated. Three coating materials, tri-n-octylamine, tri-n-hexylamine, and Amine 220, gave a good reversible response to HCl injected. Amine 220 resulted in the largest change in the crystal frequency and showed good adherence to the crystal. This substrate was selected for further testing.

The 9 MHz coated with Amine 220 was exposed to several levels of SO₂ to determine if sulfur-containing compounds would cause interferences in the detection of HCl. The results of this experiment are presented in Table 2. Repeated injections of aqueous solutions of HCl containing as much as 500 ppm NaCl (weight/volume) showed no effect from the presence of the inorganic salt.

Because of the sensitivity and specificity of the crystal with the Amine 220

coating, it was chosen for use in this system and used in all other studies. Amine 220 is a commercial product available through Pfaltz and Bauer, Stamford, Connecticut. Its chemical name is 2-(8-heptadecenyl)-2-imidazoline-1-ethanol.

The next task was to interface the detector to the furnace in which HCl (or HBr or HI) was to be generated from halogenated organics in the aqueous sample. Initial investigations involved injection of aqueous solutions into a heated quartz tube coupled to the detector cell by simple ground glass fittings. Using this configuration, injections of laboratory air produced large responses. It was determined that this was due to "thermal shock"; that is, rapid expansion of the injection in the heated quartz tube. Moving the detector cell further away to minimize this effect resulted in condensation of water on the crystal. Heating the crystal to prevent condensation caused the Amine 220 to bleed from the crystal which changed the response characteristics and caused a serious drift in the baseline. It was necessary, therefore, to introduce a component in the system between the oven and the detector which would remove water from the carrier gas stream.

Table 1. Results of Coating Selection Experiments

Coating Material	Detector Response ^a 1 mL H ₂ O	Detector Response ^a 1 mL H ₂ O + 500 µg HCl
Quadrol	9	15
Triphenylamine	3	3
Triethanolamine	10	40
4-Aminoacetanilide	17	19
Triethanolamine-HCl	3	6
Tri-n-octylamine	1	280
Tri-n-hexylamine	3	110
Triethylenetetramine	3	3
L-Ornithine-HCl	18	21
Amine-220	18	960

^aChange in frequency (Hz).

Table 2. Results of Exposure of Amine 220-Coated Crystal to SO₂

Amount SO ₂ Injected ppm (v/v)	Detector Response ^a 5 mL	% Frequency (Hz) 5 mL + SO ₂
100 (1.3 µg)	360	368
1.0 (0.013 µg)	360	364
0.1 (0.0013 µg)	360	363

^aThis represents an injection of 5 mL of laboratory air. No attempt was made to remove chlorinated compounds from the sample. Response is presumed to be due to background levels of HCl in the laboratory.

The first approach investigated was the use of a trap containing a desiccating material between the oven and the detector. Absorbance of water by calcium carbide resulted in the formation of acetylene, which seemed to strip the coating from the crystal; therefore, this approach was abandoned.

The applicability of phosphorous pentoxide was evaluated next. Although water was effectively removed by this technique, HCl was also trapped. Heating the trap to 95°C did not result in the release of HCl, and this technique was also abandoned. Anhydrous magnesium perchlorate was investigated next. Water and HCl were both trapped and HCl was released slowly when the trap was heated to 195°C. The response of the detector using this material was not reproducible. Water and HCl were both irreversibly absorbed by calcium sulfate trap.

Since trapping water on a solid material was not successful, the applicability of a concentrated sulfuric acid scrubber was investigated. The first scrubber configuration which was evaluated was constructed from a vertical glass tube packed with glass beads coated with sulfuric acid. The breakthrough capacity of the scrubber was evaluated by placing a tube containing calcium sulfate downstream of the scrubber and repeatedly injecting 0.1 mL of distilled deionized water into the system. The glass beads were coated with fresh H₂SO₄ after each injection. After 20 injections totaling 2 g of water, the calcium sulfate tube showed no weight gain. This demonstrates that the efficiency of the scrubber for water was greater than 99.9 percent. Injections of aqueous solutions of HCl yielded a minimal response. When the output of the detector was displayed on a chart recorder, a low broad peak was observed. This suggests that the HCl was being absorbed by the scrubber and gradually bled off by the action of the carrier gas.

On the assumption that this problem was caused by the large dead volume of the scrubber, another configuration was designed and tested. This scrubber was constructed from a micro volume impinger filled with sulfuric acid. A significant detector response was observed with the injection of 0.1 mL of distilled, deionized water indicating that the capacity of the scrubber had been exceeded. Use of a larger volume scrubber produced the same results. Therefore, a modification of the original system must be evaluated for incorporation into the instrument.

Finally, the efficiency of the conversion of chlorinated organics to HCl was investigated. Using an oven temperature of 600°C and an oxygen flow rate of 60 mL/min, aqueous solutions of HCl and CHCl₃ were injected into the system. Chloroform solutions were prepared at one-third the concentration of HCl solutions so that injections of equal volumes should produce the same response. Over the three orders of magnitude that the system was evaluated, the response to chloroform was consistently 10 percent of that expected based on analysis of HCl. To improve the sensitivity of the instrument, the efficiency of the conversion step must be improved.

Conclusions

Funding constraints made it impossible to evaluate additional parameters and assemble a working unit.

At the time work was terminated, the coated piezoelectric crystal detector had been demonstrated to be sensitive enough to fulfill the original grant objectives. Coated with Amine 220, the crystal is capable of detecting approximately 100 pg of HCl. The detector was also demonstrated as being insensitive to as much as 500 ppm (weight/volume) of sodium chloride and as much as 1.3 µg SO₂.

With this detector system, sample pre-concentration is not required and the analysis from start to finish is only about five minutes. Additional development of this system may provide USEPA with a significant improvement in TOX methodology and an instrument which provides rapid, reliable data on the levels of chlorinated organics in aqueous samples.

Judith A. Gebhardt is with Gulf South Research Institute, New Orleans, LA 70186.

Stephen Billels is the EPA Project Officer (see below).

The complete report, entitled "Direct Determination of Total Organic Chlorine in Water Without Preconcentration," (Order No. PB 84-129 121; Cost: \$8.50, subject to change) will be available only from:

National Technical Information Service

5285 Port Royal Road

Springfield, VA 22161

Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

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