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## Note

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# Temperature selection for chlorinated hydrocarbon reduction for the Hall electrolytic conductivity detector

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The Hall electrolytic conductivity detection system (HECD) has been used in determinations for which the HECD response factor must be equivalent for several chlorinated compounds[1,2]. Consistent with this equivalence, Lopez-Avila and Northcutt[3] stated that the response of the HECD in the halogen mode was roughly proportional to the number of chlorine atoms present[3]. Also, we have found the HECD response, relative to a response standard, to be directly related to the amount of organic chlorine for gas chromatographic (GC) eluates[1]. The proportional relationship allows for chlorinated hydrocarbon determinations using response factor calibration, which does not require identical reference materials for each analyte nor analyte identification[1]. Similarly, Nulton *et al.*[2] reported total organic halide concentrations for environmental samples using the HECD and approximated HECD response factors for several toxicants.

All the HECD measurements described above require an equivalent HECD response factor for organic chlorine from the measured chlorinated analytes, and therefore reproducible reaction of organic chlorine to hydrogen chloride prior to HECD conductometry. However, the extent of analyte reduction in HECD catalysis is temperature dependent and affects the HECD response factors. Criteria for HECD reactor temperature selection have been studied, based upon optimum measured conductivities (see for example ref. 4), but reaction efficiency has not been well characterized.

This paper presents data on temperature dependencies of analyte reductions in the HECD for chlorinated hydrocarbons. The reactor temperatures required for complete analyte degradation should generally be exceeded in determinations which require equivalent HECD response factors for organic chlorine. Additionally, degradation temperature dependencies could allow for judicious selection of temperatures, perhaps providing discrimination against some analytes and thereby enhancing selectivity[5].

## EXPERIMENTAL

### *Reagents*

Chlorinated hydrocarbons were purchased from Aldrich: 1-chlorooctane (1COA, 99% pure), 1,2,3-trichloropropane (TCPrA, 99+% pure), 1,5-dichloropen-

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tane (DCPeA, 99% pure), 1-chlorobenzene (CB, 99% pure), 1,2,4-trichlorobenzene (TCB, 99 + % pure), hexachlorobutadiene (HCBD, 98% pure) and hexachlorocyclopentadiene (HCCPD, 98% pure). Reference solutions were provided by the U.S. Environmental Protection Agency: 1,2-dichlorobenzene (1,2-DCB, 99.8% pure), 1,3-dichlorobenzene (1,3-DCB, 99 + % pure), 1,4-dichlorobenzene (1,4-DCB, 99.9% pure), 2,4,6-trichloroaniline (TCAn, 99% pure) and polychlorinated biphenyl 1016 (PCB 1016). Resi-analyzed grade *n*-hexane was purchased from J. T. Baker.

*Procedures*

Solutions of the twelve substances were prepared at concentrations ranging from about 30 to 100 μg/ml. Class A volumetric glassware and *n*-hexane were used for all dilutions.

A Tracor Model 560 gas chromatograph equipped with a Tracor Model 700A HECD was used with a 2 m × 2 mm I.D. glass column, packed with 3% OV-17 on 100/120 Supelcoport. The outlet from the HECD reactor was connected to either the membrane separator or a jet separator GC–mass spectrometry (MS) interface for a Hewlett-Packard Model 5980A mass spectrometer (GC–reactor–MS). The mass spectrometer used electron impact ionization at 70 eV. Airco-grade 4.5 helium was used as the carrier gas at 25 ml/min. Airco-grade 4.5 hydrogen with a hydrocarbon trap was used as the HECD reactor gas at 40 ml/min, a typical hydrogen flow-rate. The nickel catalyst reactor temperature was varied from 250 to 1000°C, the HECD base temperature was 250°C and the GC injector temperature was 250°C.

A Hewlett-Packard Model 3390A integrator was used to measure total ion chromatogram (TIC) peak areas and retention times. Mass ranges monitored by the TIC were from 50 to 300 *m/z* except for PCB 1016 which was monitored from 50 to 400 *m/z*. PCB peak areas included all eluted PCB isomers. A Bell and Howell Model 5-154 Datagraph oscillograph recorded mass spectra.

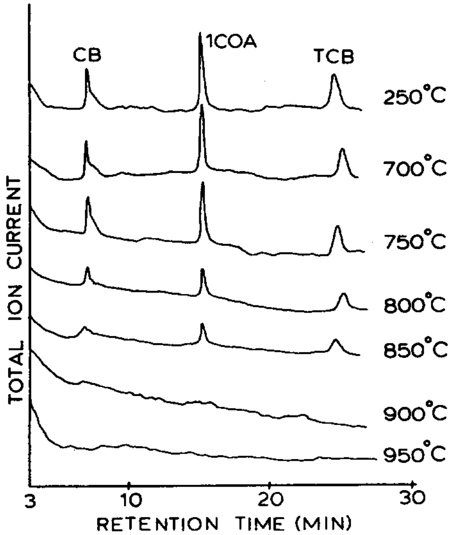

Fig. 1. Total ion chromatograms measured by the GC–reactor–MS system at reactor temperatures from 250 to 950°C. The GC temperature program increased from 30 to 75°C at 4°C/min after a 5 min isothermal period at 30°C.

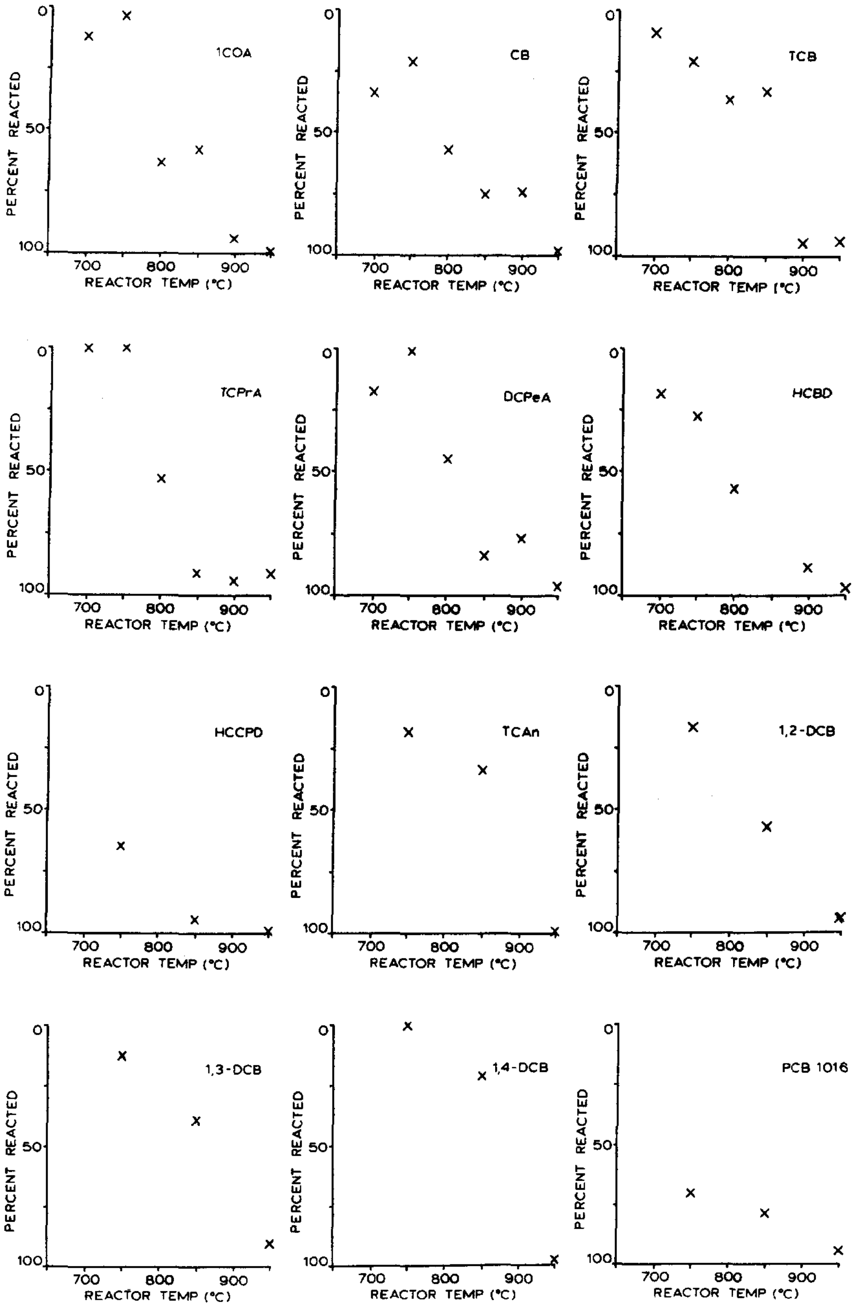

Fig. 2. Percent analyte reacted in HECD *vs.* HECD reactor temperature for chlorinated hydrocarbons.

## RESULTS AND DISCUSSION

Chlorinated hydrocarbon solutions were injected into the GC–reactor–MS system which contained the membrane separator GC–MS interface. Analytes which were not reduced in the HECD reactor, crossed the membrane and were measured by the mass spectrometer and recorded as a total ion chromatogram (Fig. 1). Polar, low molecular weight degradation products, *e.g.* hydrogen chloride, do not readily cross the membrane. As the reactor temperature was increased from 250 to 950°C, the TIC peak areas for the analytes are diminished below baseline noise levels (Fig. 1); no reaction occurs at 250°C. Fig. 2 shows the percent analyte reacted, relative to the TIC peak areas at 250°C, as a function of reactor temperature for the twelve substances: these data are sufficient for selection of temperatures for complete analyte reduction. Several of the chlorinated hydrocarbons were not completely reduced below 950°C, and their compared reduction yields varied greatly at 800°C. Thus, HECD response factors are not constant for all chlorinated hydrocarbons at catalysis temperatures lower than 950°C.

To corroborate these results, the GC–reactor–MS system was also used with a jet separator GC–MS interface. The jet separator allowed hydrogen chloride as well as other degradation products to pass into the mass spectrometer. Measurements of chlorinated hydrocarbon eluates from the HECD reactor at 950°C produced mass spectra illustrated by Fig. 3 after background subtraction. The mass spectra correspond to hydrogen chloride without the presence of other reduction products at higher masses[6]. Therefore, analyte reduction to hydrogen chloride is quantitative at 950°C. This is consistent with the assertion that in the halogen mode hydrogen chloride and methane result as HECD reactor products for chlorinated hydrocarbons: methane does not give an HECD response under normal operating conditions[5]. Therefore, the HECD response factor for organic chloride is equivalent for these chlorinated hydrocarbons at reactor temperatures exceeding 950°C since the organic chlorine is quantitatively reduced to hydrogen chloride.

These data indicate that determinations which require the same HECD response factor for organic chloride from different chlorinated hydrocarbon analytes should use a reactor temperature of at least 950°C unless another temperature is properly justified. Other analyte compounds could be evaluated with GC–reactor–MS systems to similarly identify reactor temperatures needed for complete analyte degradation.

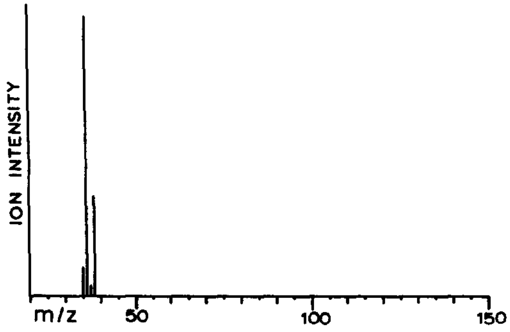

Fig. 3. Mass spectrum of HECD reactor effluent after injection of TCPrA.

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