

Destruction of highly chlorinated pesticides and herbicides using the CerOx process

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Abstract

The first commercial scale CerOx System 4 unit at the University of Nevada at Reno was used to destroy surplus highly chlorinated pesticides and herbicides from the University's agricultural departments. The non-thermal process, using an electrochemically generated metal ion oxidant, was used to destroy chlordane, kelthane, permithrin and a mixture of 2,4-D and 2,4,5-T with their dioxin impurities. The process data showed destruction efficiencies >99.995% for the chlorinated materials and >99.9% for some remaining non-chlorinated ("inert") components of the commercial product mixtures.

Introduction

At the present time, incineration is the generally used method for destruction of organic waste materials that are generated by industry. The chemistry and physics of existing thermal processes, particularly incineration, are such that the production of dioxin type materials is obligatory given the process conditions. The standard "fix" for this open-ended technology has been the addition of more back-end processing including secondary burners, precipitators, wet scrubbers and baghouse filters. The equipment train, required to meet regulations, is a complicated and expensive processing system that still operates mostly outside of regulatory specifications.

The CerOx process, licensed from the Pacific Northwest National Laboratory (PNNL), is part of the family of technologies that includes metal-ion-catalysed electrochemical processes for organic destruction. The underlying chemistry had been described in the 1960's and has been reviewed with a historical perspective describing applications over a period of 17 years by the early workers at PNNL. The earliest application of the catalysed electrochemical processes at PNNL was to accelerate the dissolution of plutonium oxide from solid mixed transuranic oxides recovered from reactors.

The CerOx process involves the reaction of a high oxidation state metal ion with an organic material to convert the organic carbon to carbon dioxide, carbon bound heteroatoms to their respective oxidised species (e.g., carbon bound nitrogen to nitrate) and hydrogen ultimately to water. The processes operate near room temperature and at atmospheric pressure in an aqueous acid electrolyte. The processes afford virtually complete destruction of the organic materials since the oxidised metal-ion mediators are thermodynamically powerful and kinetically active oxidising agents and, important for regulatory concerns, the organic materials and reaction intermediates are confined in the electrolyte until the destruction of the organic materials is complete.

In the process, the overall chemical reaction that results in the destruction of the organic waste materials is approximately equivalent to the combustion reaction, except the product from chlorocarbon destruction is molecular chlorine rather than hydrogen chloride. Unlike incineration, the process is comprised of four distinct chemical reactions/processes that are temporally and physically separate. The reactions/processes are: organic destruction by Ce(IV); regeneration of the Ce(IV) oxidant; the cathode reaction, reduction of nitric acid to nitrous acid; and, the recovery of nitric acid from the cathode reduction product. Since the cerium is not consumed in the process it is a catalyst, which is electrochemically regenerated.

Since, the CerOx process is performed in a series of tanks and pipes, the CerOx process is classified as a tank system. As a tank system, the CerOx process is exempt from RCRA regulation as confirmed by EPA. In agreement, the regulators in 40 States have stated that the CerOx process does not require an EPA RCRA permit (Type B Permit). The conditions in the process are such that the reaction conditions, e.g., high temperature, needed for the synthesis of dioxins from chlorocarbon feed materials are never attained making the CerOx process a dioxin destroyer, not a dioxin maker.

The process and process chemistry

The process operations and process chemistry are related such that it is easier to describe the chemistry in terms of the application rather than separated from the use. The process schematic of the CerOx System 4 at the University of Nevada at Reno is shown in Figure 1. The process involves electrochemical cells for the generation of the active cerium(IV) oxidant at the anode, a liquid phase reactor for primary organic destruction, a gas phase reactor to destroy any fugitive emissions from the liquid reactor and an acid gas scrubber for removal of acid gases prior to venting to the atmosphere.

The catholyte loop indicated in Figure 1 is designed to recover nitric acid from the nitric acid reduction products that are the result of the cathode reaction, a necessary part of any electrochemical process. The cathodic processes are separated from the anodic (waste destruction) processes by a fluorocarbon membrane, which confines the waste materials to the anolyte loops.

In operation, the organic waste materials are injected into the oxidising electrolyte through an ultrasonic mixer, which emulsifies immiscible organics into the aqueous anolyte to maximise the contact area between the organic and the cerium (IV) oxidant. The organic/oxidant mixture is fed into the liquid reactor for completion of the oxidation reactions that convert the organic materials to, primarily, carbon dioxide and water while carbon bound chlorine is converted to molecular chlorine. An example destruction process is given in Equation 1 using chlorobenzene. Other carbon bound heteroatoms, such as

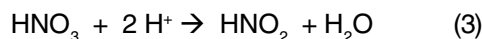


nitrogen, phosphorous and sulphur are oxidised to their respective oxyacids, i.e., nitric acid, phosphoric acid and sulphuric acid. As implied in Equation 1, the oxygen in the CO_2 product comes from water which makes the destruction reaction approximately thermoneutral. This, in turn, eliminates the potential for thermal runaway reactions in the liquid reactor.

The active Ce(IV) oxidant is regenerated from the reduced Ce(III) by re-oxidation in the electrochemical cell according to Equation 2.



The electro-chemical regeneration and recycling of the cerium oxidant makes the cerium a true catalyst in the process. The corresponding cathode reaction, the reduction of nitric acid to nitrous acid, is shown in Equation 3.



The cathode reaction is the major exothermic reaction in the process but, since it only occurs when dc power is applied, it also does not pose a thermal runaway potential. The electrochemical basis of the process makes the process absolutely controllable since it can be shutdown with the flip of the power switch as is done automatically should an upset occur.

The nitrous acid product, HNO_2 , from the cathode reaction, Equation 3, disproportionates in solution to produce nitric acid and nitric oxide, NO. The gaseous NO is oxidised with atmospheric oxygen to NO_2 , which is then dissolved in water to make nitric acid. These oxidation/absorption processes recover much of the nitric acid consumed in the cathode reaction.

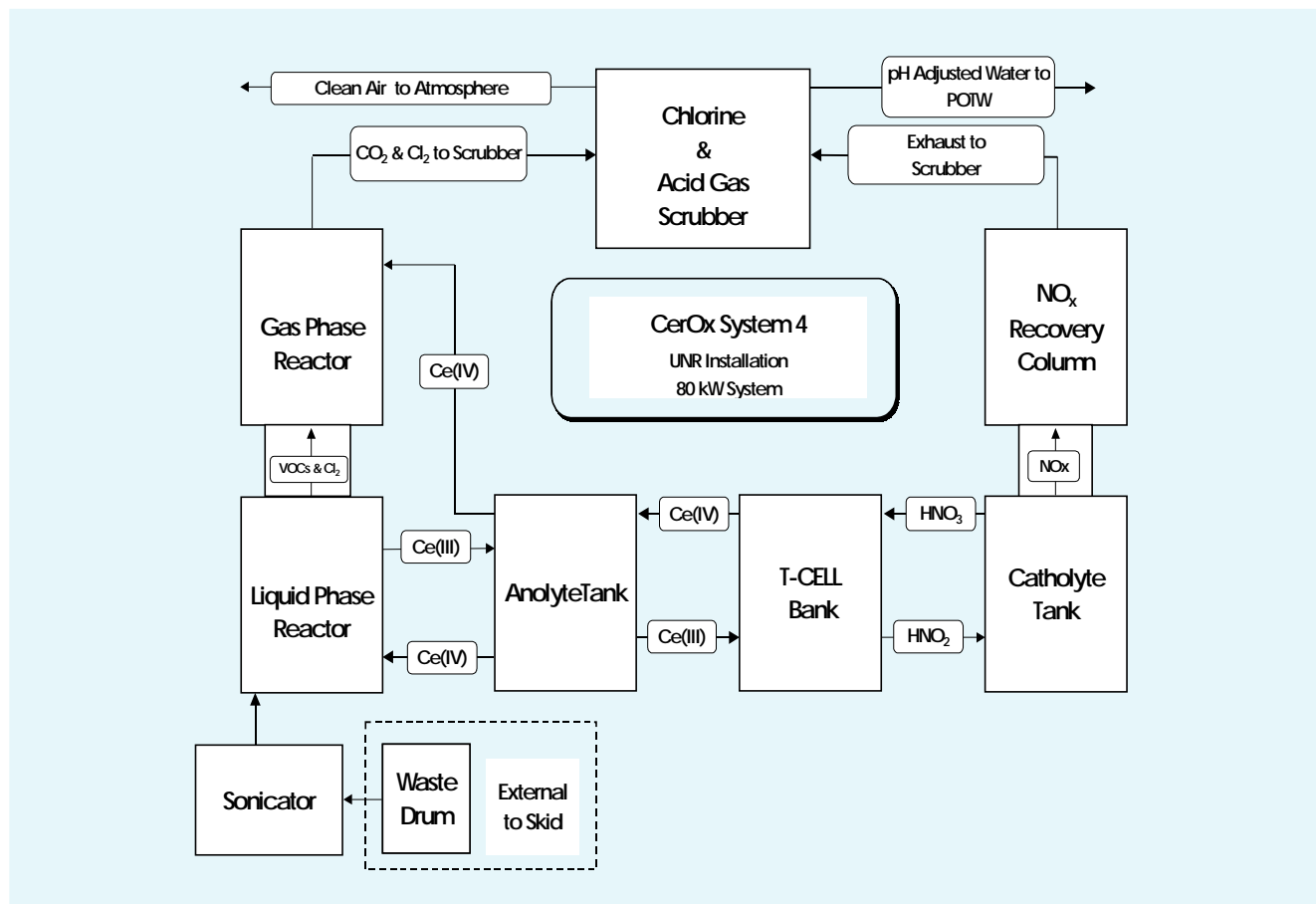


Figure 1. Process schematic of CerOx System 4

The System 4 has a fixed cerium(IV) production capacity and the mass throughput is a function of the electron demand of the waste materials. While nominal capacity of the 80kW system shown in Figure 1 is approximately 1/2 drum of organic waste, containing 50% water, per day, the actual throughput is a function of the electron demand of the waste materials. For example, more highly reduced alkanes require more Ce(IV) per unit mass than oxygenates or chlorocarbons so their mass throughput per unit time will be lower.

Experimental

The destruction tests were performed using a System 4 at the University of Nevada in Reno. The unit was operated at steady state with an electrolyte temperature running between 90 and 95°C at atmospheric pressure. Atmospheric pressure in Reno is about 0.85 atm. The test materials were surplus chemicals stored on the UNR campus by the various user departments. The materials tested are listed in Table 1.

Table 1. Chlorocarbon test materials used in the present study

Material	Formula	Manufacturer	% Active Ingredients	% Water in Feed
Kelthane	C ₁₄ H ₉ Cl ₅ O	Rohm & Haas	42%	50%
Permethrin (Ambush)	C ₂₁ H ₂₀ Cl ₂ O ₃	ICI	50%	50%
Weed-B-Gone 2,4-D 2,4,5-T	C ₈ H ₆ Cl ₂ O ₃ C ₉ H ₇ Cl ₃ O ₃	Chevron Chemical	21.4% 10.0%	50%
Chlordane	C ₁₀ H ₆ Cl ₈	Ortho	71%	50%

The System 4 was operated using normal procedures that include building of the Ce(IV) level in the anolyte to a working level during which the temperature of the process fluids was also raised to a minimum of 85°C prior to addition of the organic to the liquid phase reactor. The organic materials were metered into the liquid phase reactor at a rate that approximately matched the electrochemical make rate of Ce(IV).

The composition of the off-gas streams from the liquid phase and gas phase reactors and the vent to the atmosphere from the acid gas scrubber were monitored using a ThermoStar™ gas analyser on loan from Pfeiffer Vacuum. The ThermoStar™ analyser employs a glass capillary inlet, which allows for sampling at atmospheric pressure. The capillary produces the necessary pressure drop so that a quadrupole mass detector can be used for direct detection and measurement of gas phase components. The ThermoStar™ analyser can detect gas phase species down to ppb levels under "good" circumstances, e.g., no interfering materials, low instrument background levels, precise calibration with known quantities of materials, among others. Routine operation to low ppm of materials is fairly routine.

The mass analyser was also used to determine the gas flow rate of the exhaust stream through measurement of the argon content of the stream. The process gas stream was injected with a measured flow of argon gas, which was fed into the process gas stream ahead of all of the sampling ports to provide for a measure of the mass flow of the exhaust gas.

Results

The exhaust gas flows from the liquid reactor and the gas phase reactor were monitored for gas phase organic constituents with particular emphasis on the detection of any of the chlorinated pesticides and herbicides using the Pfeiffer Vacuum gas analyser. As no pure samples of these highly chlorinated materials were available at test time, the level of the chlorinated active ingredients detected would be estimated based upon the ion current measured.

The mass spectra of each of the chlorinated materials were obtained from the National Institute of Standards and Testing (NIST) website (<http://webbook.nist.gov/chemistry>) to locate the expected m/z values for each component. The fact that each of the target components of the analysis had multiple chlorine atoms would assist in identifying any peaks associated with the herbicide or pesticide owing to the existence of the 2 chlorine isotopes in the (approximate) 3:1 ratio for ³⁵Cl and ³⁷Cl. The isotopic distribution for poly-chlorinated materials provides a unique fingerprint for their identification.

Representative mass spectra are shown in Figure 2 for Ambush™ (permethrin), Figure 3 for Kelthane™ (dicofol, a DDT variant), Figure 3 for Weed B Gone™ (21.4% 2,4-dichlorophenoxyacetic acid & 10% 2-(2,4,5-trichlorophenoxy) propionic acid [Silvex™]) and Figure 4 for chlordane, a highly chlorinated material. These spectra were all obtained from the gas phase reactor off-gas stream. In general, the recorded spectra are clean of chlorinated organics that are indicated in the NIST reference spectra for each of the materials.

As seen in Figures 2 through 5, the exhaust gas stream consists mainly of water, CO₂, nitrogen (N₂), oxygen (O₂) and argon. Oxygen can be in excess of nitrogen since O₂ is also an anodic product formed through the oxidation of water, an anodic co-process. In addition there is a mass marker at m/z = 69 due to CF₃⁺ left over from a fluorocarbon mass calibration standard.

Mass spectra of organic materials often exhibit a large number of peaks owing to the fragmentation of the molecule upon electron impact ionisation. The resulting patterns are characteristic of each molecule. The convention regarding the cataloguing of mass spectra assigns a value of 100% to the largest peak; the other peaks are then reported as a per cent of the largest peak. The components of Weed B Gone™ and Ambush™ have their 100% peaks with m/z ≤ 200, the maximum range of the gas analyser. None of the 100% peaks were detected; this lack of detection allows an assignment of 0.1 ppm as an upper limit for their concentration in the gas phase. Since the 100% peaks for Kelthane and chlordane have m/z values >200, they could not be observed even if present. Their known fragment peaks, as shown in the NIST spectra, could not be identified in Figures 3 or 5. On this basis, their upper limit in the gas phase is estimated at 1 ppm. With these values for the upper limit concentrations in the exhaust stream, the destruction levels shown in Table 2 were calculated.

Table 2. Chlorinated materials: Mass flow and destruction efficiency

Material	Gas Flow	Gas Phase Concentration		Feed Rate	Destruction
	l/min	ppm	µg/min	g/min	%
Chlordane	10	1	184	3.4	99.995
Ambush™	14	0.1	24	1.85	99.998
Kelthane™	6	1	99	4.8	99.998
2,4-D	10	0.1	10.0	0.6	99.998
2,4,5-T	10	0.1	12.1	0.3	99.996

Commercial formulations of the pesticide and herbicide materials listed in Tables 1 & 2 were fed as 50% emulsions in water. These mixtures also contained kerosene and suitable surfactants to maintain the emulsions. The presence of these inert ingredients was clearly evident particularly in Figure 5 with the many peaks in the $m/z = 50$ to 95 range. The peak shapes and their spacing at $m/z = 14$ is the classic signature for aliphatic hydrocarbons spaced every CH_2 grouping (Balzers Instruments, Partial Pressure Measurement in Vacuum Technology, BG 800 169 PE (9610)).

Conclusions

The absence of detectable peaks for the tested chlorinated pesticides and herbicides allows for the establishment of minimum destruction efficiencies on the order of 99.995% for these materials with the CerOx process. The operation of the Ce(IV) based oxidation chemistry at atmospheric pressure and low temperature, $< 100^\circ\text{C}$, precludes the formation of the more toxic dioxins and (benzo)furans during the destruction process.

It is intended to continue and expand this study in the near future to include destruction efficiencies on the order of 99.995% for these materials with the CerOx process. The operation of the Ce(IV) based oxidation chemistry at atmospheric pressure and low temperature, $< 100^\circ\text{C}$, precludes the formation of the more toxic dioxins and (benzo)furans during the destruction process.

It is intended to continue and expand this study in the near future to include destruction of PCB's, chlorinated dioxins and (benzo)furans, additional pesticides and herbicides, including parathion, Diazinon®, and more volatile persistent recalcitrant chlorocarbons like PERC (perchloroethylene) methyl chloroform and TCE (tetrachloroethylene).

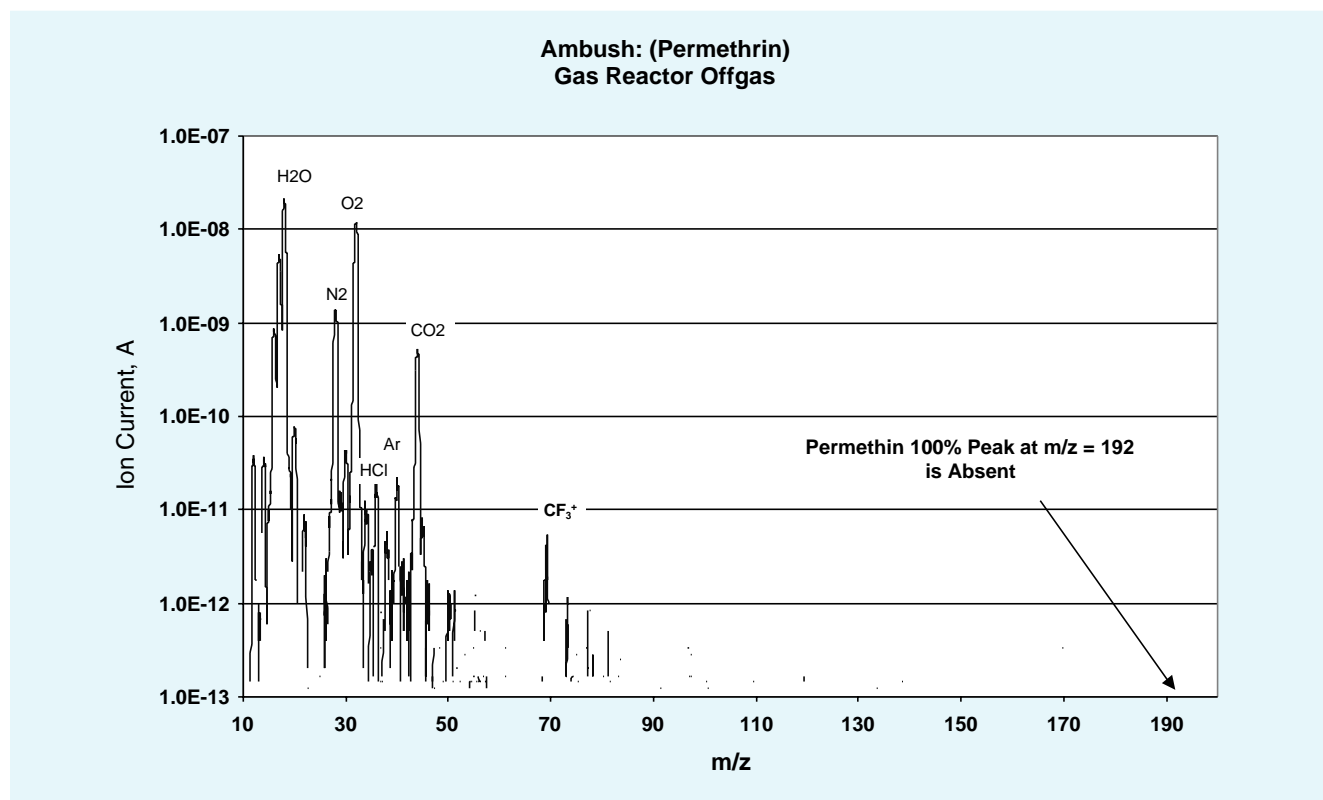


Figure 2. Ambush (permethrin) mass spectrum

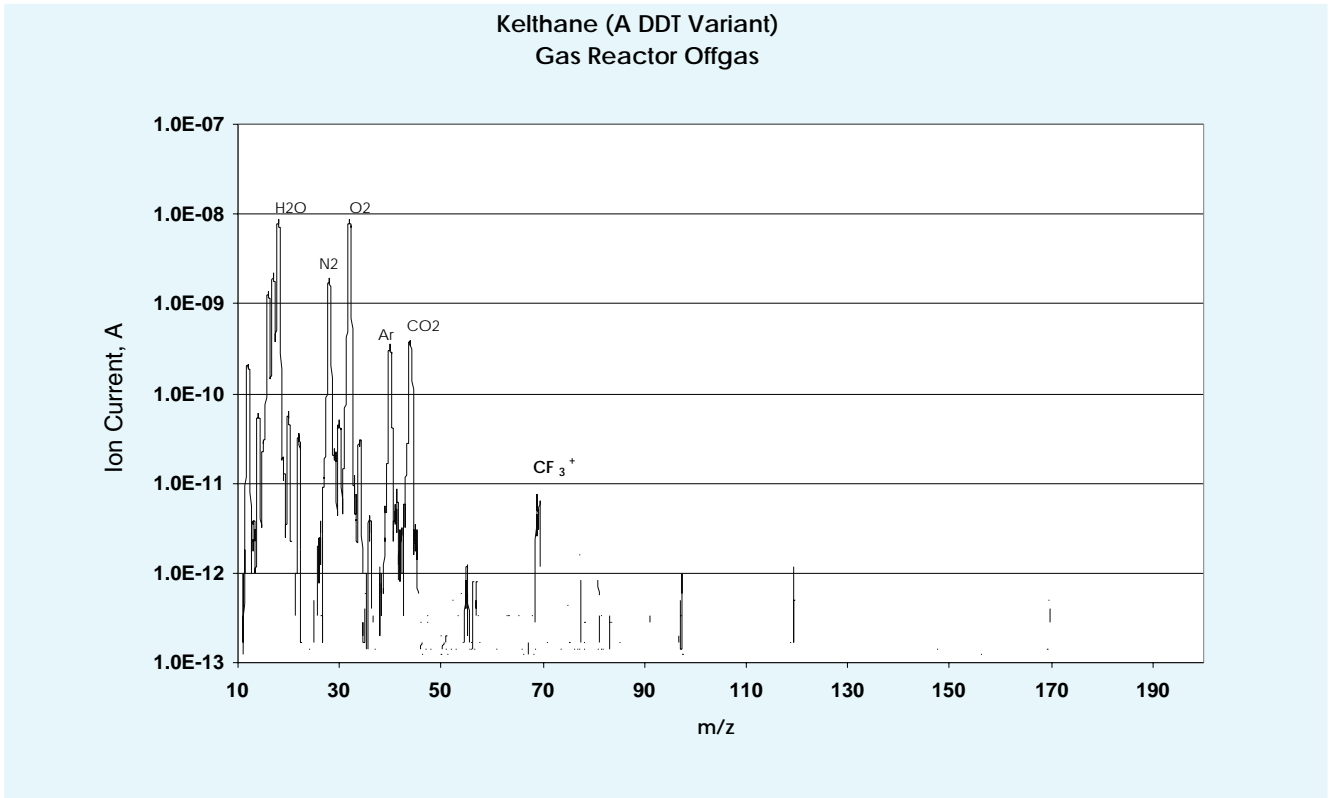


Figure 3. Kelthane mass spectrum

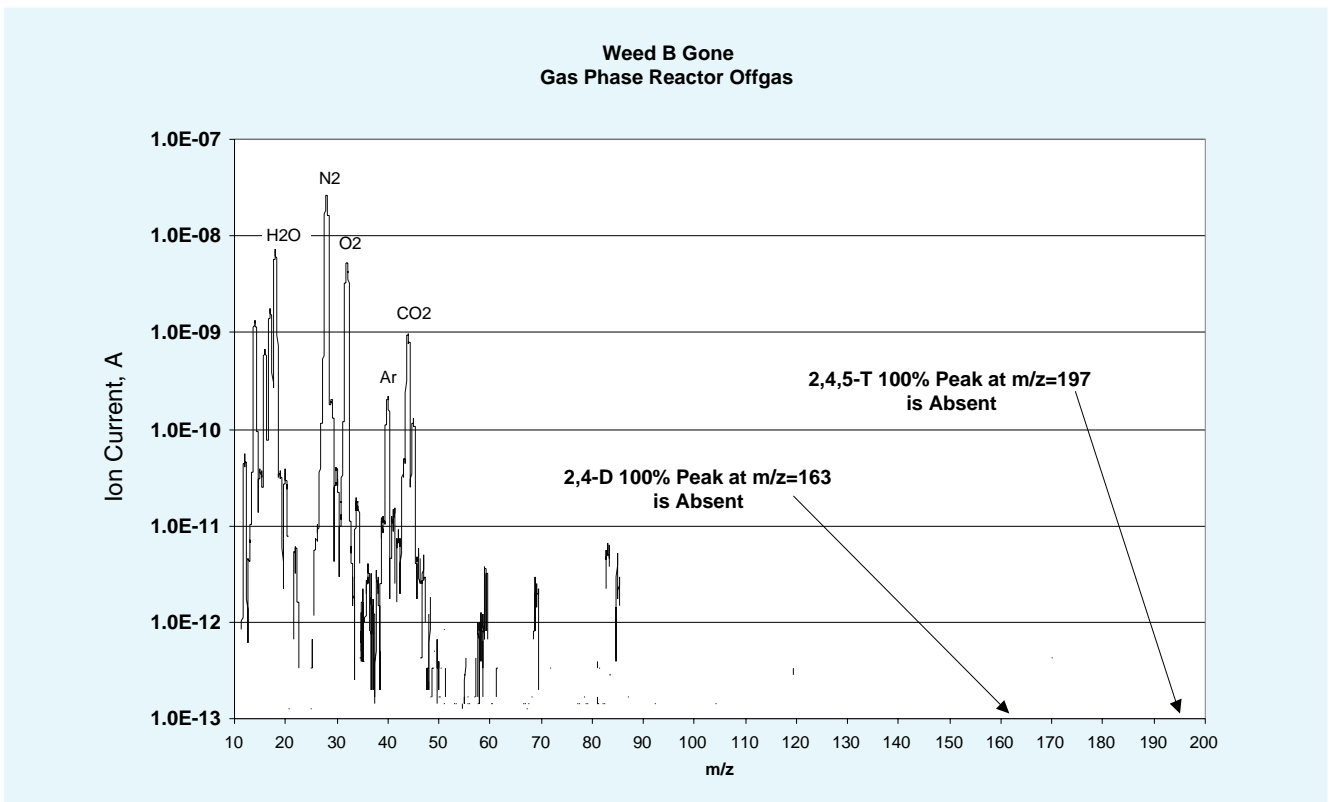


Figure 4. Weed B Gone mass spectrum

Chlordane
Gas Reactor Offgas

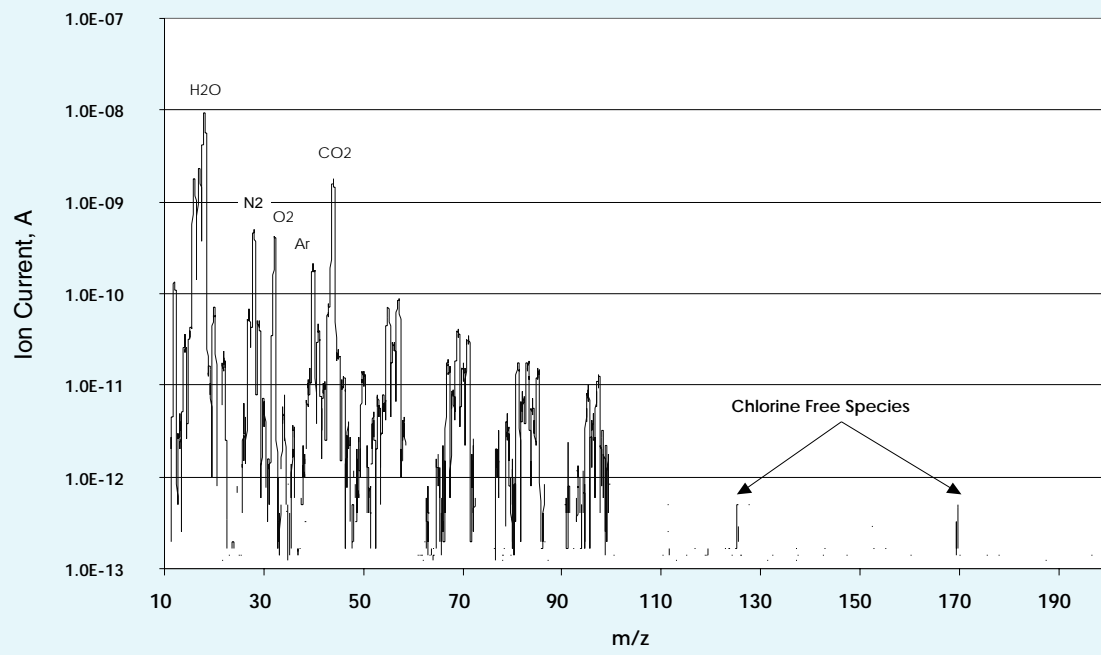


Figure 5. Chlordane mass spectrum