

## Destruction of Halogenated VOCs Using Premixed Radiant Burner

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### INTRODUCTION

Alzeta Corporation has developed a natural-gas-fired thermal oxidizer to provide emission control for industrial exhaust streams where stringent emission limits of volatile organic compounds (VOCs) are required. Measurements made with assistance from the U.S. Environmental Protection Agency (EPA) at Research Triangle Park, North Carolina, show destruction efficiencies (DEs) between 99.9766 and 99.9999 percent for eight common halogenated compounds. This thermal oxidizer technology utilizes an inward-fired premixed radiant burner that operates at high levels of excess air (typically 80 to 100 percent) to achieve nitrogen oxide ( $\text{NO}_x$ ) and carbon monoxide (CO) emissions below 10 ppm<sub>v</sub>, corrected to 3 percent oxygen ( $\text{O}_2$ ). A brief discussion of pertinent regulations and emissions of concern is presented. The evaluation test program is presented with results. A description of three similarly designed commercial thermal oxidizers is presented including emission test results.

### Regulations and Current Health Risk Assessments

The need for ultraclean burning thermal oxidation technology is driven by air emission regulations aimed at reducing toxic or hazardous air pollutants. On the list of 190 hazardous air pollutants proposed to be regulated by the EPA (1) are many halogenated VOCs, including carbon tetrachloride, trichloroethylene, and methylene chloride.

Halogenated compounds present health hazards and are more difficult to fully oxidize relative to non-halogenated compounds (2). Further, combustion of these compounds may result in the formation of products of incomplete combustion (PICs) that may be more toxic than the original compounds; dioxins and furans, for example (3). A permitted thermal oxidizer must meet the DE limit set for the given industrial process (typically 95 to 99 percent of the untreated VOCs must be oxidized). If a hazardous air pollutant is present, a screening for health risk is also required. Table 1 lists several compounds and emission trigger limits used by the San Francisco Bay Area Air Quality Management District (BAAQMD). For reference, the BAAQMD trigger limit for carbon tetrachloride is 2.1 kg/yr

(4.6 lb/yr). This corresponds to an emission level of less than 0.022 ppm<sub>v</sub> in a 28,322 L/min (1,000 scfm) air stream flowing continuously.

### Future Title III Proposals

Future air toxic regulations are expected from the EPA as part of Title III, Section 112 of the Clean Air Act. Maximum Available Control Technology (MACT) standards for emission limits are scheduled to be set for various source categories, including chemical manufacturing facilities, ethylene oxide sterilization facilities, gasoline distribution stations, and dry cleaners.

### Dioxins, Furans, and Formation Mechanisms

Of particular concern is control of polychlorinated dibenzodioxins and dibenzofurans (PCDDs/PCDFs). These compounds are also potentially formed from oxidation of gas-phase halogenated VOCs (4). Table 1 shows a BAAQMD-established health risk trigger level of  $5.4 \times 10^{-7}$  kg/yr ( $1.2 \times 10^{-6}$  lb/yr) for these compounds.

There are 75 PCDD congeners and 135 PCDF congeners, all referred to generically herein as "dioxins," the most toxic of which is 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). This compound is used as a toxicity standard. The emission of these compounds from an oxidation process may result from any of the following: 1) the presence of dioxin in a feed stream that is not fully oxidized; 2) the formation of the dioxin from PICs; and 3) "de novo" formation from dioxin constituents catalyzed from solid surface contact. PICs that are dioxin precursors are typically chlorinated aromatic hydrocarbons. At temperatures above 1,000°C (about 1,800°F) the likelihood for formation and survival of dioxins is very low, with destruction efficiencies over 99.99 percent. De novo formation occurs typically in low temperature regions of between 230 to 400°C (450 to 750°F) with the following components: oxygen-, hydrogen-, carbon-, and chlorine-containing compounds with particulate or metal wall surfaces to promote catalytic reactions (3,4,5,6).

## OXIDIZER TESTING AND COMMERCIAL APPLICATIONS

### Evaluation Test Program

**Objective.** Recognizing the difficulty in oxidizing chlorinated chemicals and the potential for PIC formation, and with encouragement from the South Coast Air Quality Management District (SCAQMD) and funding from the Gas Research Institute (GRI), Alzeta provided Acurex Environmental Corporation (Acurex) with an inward-fired thermal oxidizer system for VOC destruction testing. The testing was performed by Acurex under the guidance of EPA's Control Technology Center (CTC) at Research Triangle Park, North Carolina. CTC is set up jointly by EPA's Office of Air Quality Planning and Standards (OAQPS) and Office of Research and Development (ORD) to assist state and local environmental agencies to solve specific air pollution problems.

Interest in testing Alzeta's inward-fired burner technology stemmed from SCAQMD's continuing support of emission abatement technologies that can simultaneously reduce nitrogen oxides (NO<sub>x</sub>) and VOC emissions, without generating other harmful PICs. Thermal treatment technologies capable of achieving this goal offer industries unable to eliminate halogenated VOCs from their chemical processes (such as electronics and pharmaceuticals) with an another emission control option.

**Burner Description.** The thermal oxidizer sent for testing (Figure 1) was the twin of a commercial system used for destroying BTEX (benzene, toluene, ethylene, and xylene) compounds at soil remediation sites. Operating at a control temperature of approximately 871°C (1600°F), this particular burner can process up to 2,832 L/min (100 scfm) of gaseous process media. The burner is approximately 25.4 cm (10 in.) in diameter and 61 cm (24 in.) long. In this application the inward-fired burner typically operates at a surface firing rate of approximately 157 kW/m<sup>2</sup> (50,000 Btu/hr-ft<sup>2</sup>) which corresponds to a firing rate of 73.3 kW (250,000 Btu/hr) for this burner.

With the inward-fired radiant burner geometry, the burner is formed on the interior surface of an annular air-fuel plenum (Figure 2) so that the radiant surface fires inwardly upon itself. Premixed air, fuel, and VOCs enter the plenum, flow through the ceramic fiber burner matrix, and combust flamelessly at the burner's surface. Due to gas-phase radiation, the ceramic fiber surface becomes incandescent and reaches approximately 982°C (1,800°F). Surface-to-surface radiation exchange results in near-adiabatic operation, resulting in stable combustion at high excess air levels (to greater than 100 percent). High excess air operation reduces flame temperatures, resulting in low NO<sub>x</sub> emissions. Since the reactants are well mixed before combusting in the oxygen-rich environment, CO and hydrocarbon (HC) emissions are typically low also.

**Test Program.** VOC destruction tests were performed using the inward-fired thermal oxidizer. With assistance and guidance from CTC for the program, a test matrix was prepared using eight VOCs (Table 2). Criteria for VOC selection included common use in industry (xylene, methylethyl ketone, and selected halogenated VOCs) and potential for formation of PICs, such as PCDDs/PCDFs. In addition to determining the VOC destruction efficiencies, criteria pollutant emissions of NO<sub>x</sub> (NO plus NO<sub>2</sub>), CO, and HCs were measured. It was decided to repeat the chlorobenzene test three times to verify reproducibility of the burner system performance.

**Sampling Methodology.** In order to achieve the specified input concentrations, VOCs were mixed with the combustion air upstream of the burner in two ways, depending on their standard states. Gaseous VOCs were metered into the combustion air through rotameters to result in concentrations specified in the test matrix. Rotameters were calibrated for the specific gaseous VOC using a soap film bubble test calibrator. Liquid VOCs were introduced by flowing a controlled portion of combustion air through an impinger system filled with the compound prior to mixing with the remainder of the combustion air. Calculations showed that saturation vapor pressures of the liquid-state compounds in air at room temperature were sufficient to yield concentrations of approximately 100 to 500 ppm<sub>v</sub>. Continuous monitoring of the VOC-laden combustion air using a flame ionization detector (FID) hydrocarbon analyzer ensured minimal fluctuations during testing. The actual amount of each liquid-state VOC expended was determined by mass loss measurements.

Stack emissions of O<sub>2</sub>, carbon dioxide (CO<sub>2</sub>), NO<sub>x</sub>, CO, and HCs were measured using continuous emission monitors (CEMs). HC measurements were based on propane. Gas temperatures were measured using thermocouples connected to system's controller displays. Stack concentrations of target VOCs and volatile PICs were determined by Volatile Organics Sampling Train (VOST, EPA Method 0030) (7) and Tedlar bag methods (EPA Draft Method 0040) (8), as appropriate. Sampling and analyzing for volatile PICs were performed for one of the three chlorobenzene tests to investigate the potential for forming PCDD and PCDF compounds during combustion. PCDD and PCDF emissions were determined by EPA Method 23 (9).

Prior to testing the specific compounds, field and combustion blanks were obtained as a matter of course for quality assurance. Samples from each destruction test were analyzed for primary organic hazardous constituents (POHCs) and PICs remaining after combustion.

**Results.** Destruction efficiency results for each test were presented in terms of nanograms of analyte found on the VOST tubes or in the Tedlar bags, and in terms of the concentration in the stack associated with the measured mass expended during the particular test.

Field blank results showed trace amounts of acetone, methylene chloride, and toluene, similar to results from daily laboratory blanks. Combustion blanks showed trace amounts of acetone and toluene, similar to the field blanks. Unexpected trace amounts of chlorinated PICs and some fluorinated and brominated compounds were also found in some POHC test results. Though they were not found in the combustion blanks, they may be due to VOST tube contamination.

Results in Table 3 show destruction efficiencies (DEs) for all POHC test conditions. DEs reported are not corrected for combustion blanks. Specifically:

**2-Butanone (MEK).** Two runs of three tests each were reported. VOST tube breakage rendered Run 2 invalid. The average DEs were 99.9998 and 99.9988 percent for Runs 1 and 3, respectively. Traces of acetone, methylene chloride, and toluene, similar to the combustion blanks, were found in both runs. Traces of chlorinated, fluorinated, and brominated compounds were present. The origin of the halogens is not known, but is possibly from the natural gas.

**Methylene Chloride.** One run of three tests was reported. The average DE was 99.9766 percent. PIC levels increased slightly, relative to MEK results. Carbon tetrachloride appeared as a PIC at approximately 0.2 ppb, probably indicating some incomplete breakdown of methylene chloride and partial rearrangement of available chlorine.

**O-Xylene.** Two runs using o-xylene at two concentrations, 36 and 61 ppm<sub>v</sub>, were conducted. Again, VOST tube breakage invalidated Test 1 of Run 2. DEs for the 61-ppm<sub>v</sub> tests were higher than for the 36-ppm<sub>v</sub> tests, perhaps due to the higher inlet concentration. Average DEs for Runs 1 and 2, respectively, were 99.9880 and 99.9996 percent.

**Chlorobenzene.** Three runs using chlorobenzene were conducted. Inlet concentrations were 50 ppm<sub>v</sub> for Run 1 and 90 ppm<sub>v</sub> for Runs 2 and 3. DEs for the 90 ppm<sub>v</sub> tests again were higher than for the 50 ppm<sub>v</sub> tests. Average DEs for the three runs, respectively, were 99.9982, 99.9998, and 99.9996 percent. Sampling and analysis of the stack gas from one of the tests indicated the presence of trace PCDDs/PCDFs. This finding is discussed below.

**Trichloroethylene (TCE).** Two runs were conducted with TCE, one at approximately 100 ppm<sub>v</sub> and the other at 500 ppm<sub>v</sub>. The average DE for both runs was 99.9994 percent. The high DE indicates effective treatment at high inlet concentrations. No significant PICs were noticed.

**Dichloroethylene (DCE).** One run was conducted with DCE. Exhaust PIC concentrations were higher than in the TCE test, but DEs were still high at an average of 99.9956 percent.

**Dichlorodifluoroethane.** Two runs were conducted with dichlorodifluoroethane (Refrigerant-12). This was introduced directly from a gas cylinder through a calibrated rotameter. Inlet concentrations were 100 and 1,000 ppm<sub>v</sub> for the two runs. The volatility of this compound required sampling with Tedlar bags. DEs for these tests were calculated using a Practical Quantitation Limit (PQL) of 0.2 ng on the column for the 1L injections. The average DE for both runs was 99.9999 percent. No significant concentrations of PICs were detected.

**Hexafluoroethane (C<sub>2</sub>F<sub>6</sub>).** Two runs were conducted with hexafluoroethane. This was introduced directly from a gas cylinder through a calibrated rotameter. As with the Refrigerant-12 tests, inlet concentrations were 100 and 1,000 ppm<sub>v</sub> for the two runs. DEs for these tests were calculated using a PQL of 0.2 ng on the column for the 1L injections. Also, as with Refrigerant-12, no POHC was detected in the Tedlar bag samples. The average DE for these runs was 99.9999 percent. No PICs were detected.

**Criteria Pollutants.** Criteria pollutant emissions (as measured at approximately 10 percent O<sub>2</sub>, wet) are shown in Table 4. In the combustion blanks, the NO<sub>x</sub> (NO plus NO<sub>2</sub>) concentration was 2.48 ppm<sub>v</sub>, and CO was 0.15 ppm<sub>v</sub>. NO<sub>x</sub> concentrations from POHC tests ranged from detectable to 2.50 ppm<sub>v</sub>. CO concentrations were similarly low, showing consistently negative values up to 1.87 ppm<sub>v</sub>. These results demonstrate the performance of the burner as a low-NO<sub>x</sub> technology. No unburned HCs were detected.

Actually, HC output consistently yielded negative values and are superseded by the VOST and Tedlar bag organic data.

**PICs.** PCDDs/PCDFs were detected in one of the chlorobenzene tests. Analysis for these PICs was performed by EPA Method 23 (9). Total PCDDs/PCDFs are shown in Table 5. While present, the concentrations (7.01 ng/Nm<sup>3</sup> corrected to 7 percent O<sub>2</sub>, total PCDDs/PCDFs) are well below the value regulated for hazardous waste incineration in the U.S. (30 ng/Nm<sup>3</sup>, corrected to 7 percent O<sub>2</sub>). This result is unexpected given the environment, because destruction is favored over formation at these temperatures (6). The burner operates at approximately 1,000°C (approximately 1,800°F) and sampling occurred at 850°C (approximately 1,560°F). Analysis of a chlorobenzene feed sample showed no PCDD/PCDF contamination, suggesting either equipment contamination or formation in the sampling train. The dioxin formation temperature window is between about 225 and 600°C (437 and 1,112°F). EPA Method 23 protocol specifies a sampling probe temperature of 110°C (230°F). The sampling probe in this case was not water-cooled, suggesting that sufficient residence time was available within the formation temperature window. However, insufficient time was available to conduct repeat tests to provide additional insight.

**Quality Assurance.** All recovery spikes for VOST measurement were within the limits of the method.

#### **Inward-Fired Thermal Oxidizer Commercial Installations**

Three commercial installations based on the inward-fired burner technology are described below. Two installations involve semiconductor-related applications and one involves soil remediation.

**NEC Electronics, Roseville, CA.** In August 1994, Alzeta installed an abatement system (Figure 3) to remove VOCs from the process air. The VOCs were primarily 1,2-dichlorobenzene, isopropyl alcohol, phenol, and methylethylbenzene. The cumulative VOC mass flow was approximately 9.1 kg/hr (20 lb/hr) in a process air stream flow rate of 28,316 L/min (10,000 cfm). The process flow diagram is shown in Figure 4. The system uses an organic concentrator to remove VOCs from the process air. The concentrator adsorbent is regenerated by counterflowing 24,000 L/min (850 cfm) heated air at approximately 176°C (350°F) through the adsorbent matrix. A regeneration heater provides the heated air stream. Desorbate concentration is typically ten times that of the process air which results in lower fuel usage by the thermal oxidizer. The VOC-laden desorbate air forms the combustion air for the thermal oxidizer which fires at approximately 733 kW (2.5 million Btu/hr). The user required continuous operation with only brief annual facility-wide shutdowns for maintenance.

**Test Results.** Independent thermal oxidizer emission tests were required to determine compliance of thermal oxidizer stack emissions with the local air pollution control district's regulations. With the thermal oxidizer on-line, three separate 40-minute tests were conducted. Sampling was performed with an on-line FID using California Air Resources Board (CARB) Method 1-100 (10). Inlet hydrocarbon concentration was monitored using BAAQMD Method ST-7 (11). Concurrently, Tedlar bags and Summa canisters were taken and analyzed using EPA Method TO-14 (12).

Destruction efficiencies for the combined concentrator and thermal oxidizer system were calculated in two ways: first, based on FID measurements of total non-methane hydrocarbons, measured as methane; and second, based on the average molecular weight of all VOCs using speciated results from batch sample analyses. Table 6 shows the DEs for the three tests based on total non-methane hydrocarbons (TNMHCs). The average DE for the three 40-minute tests was 98.38 percent, with the lowest being 98.14 percent. VOC-weighted results using speciated data showed an average DE of 98.53 percent, with the lowest at 98.255 percent. An additional test was performed to determine thermal oxidizer destruction efficiency alone. This turned out to be 99.2 percent. Portable emission analysis results showed NO<sub>x</sub> and CO emissions of 8.9 and 12.6 ppm, respectively.

**ECI Semiconductor, Santa Clara, CA.** A 14,000 L/min (500 cfm) inward-fired thermal oxidizer (Figure 5) was installed in mid-1995 to destroy xylene, contained in the process air which vents from positive and negative photoresist applicators. The thermal oxidizer operates continuously.

**Test Results.** A compliance control efficiency test was performed as a permit requirement of the BAAQMD. The process air inlet was continuously monitored during triplicate 30-minute tests for TNMHCs and CO<sub>2</sub>, using the BAAQMD combustion procedure, Method ST-7. Simultaneously, the outlet was monitored for CO<sub>2</sub>, O<sub>2</sub>, and TNMHCs using a FID. Inlet O<sub>2</sub>, CO, and methane were checked and determined to be ambient since no combustion sources were related to the processes. Stack moisture content and volumetric flow rate were measured. The DE averaged greater than 99.46 percent. Carbon monoxide concentrations were between 15.1 and 19.2 ppm<sub>v</sub>. Analysis for NO<sub>x</sub> was not performed.

**Soil Remediation Unit.** In March 1991, Alzeta supplied to an environmental remediation contractor the twin of the unit used for the EPA tests described above. The thermal oxidizer was designed to destroy BTEX emissions from a vacuum extraction system in the vicinity of an underground gasoline tank. The extracted ventilation air flow was 2,832 L/min (100 scfm), with initial hydrocarbon concentrations of 1,000 ppm<sub>v</sub>. Table 7 shows results of hydrocarbon analyses performed at the inlet and exhaust streams. Though no halogenated compounds were present, the removal of BTEX vapors to the detection limits of 0.05 ppm<sub>v</sub> was helpful in passing health-risk screening criteria.

## CONCLUSIONS

### Evaluation Test Program

The inward-fired radiant burner demonstrated effective treatment technology for halogenated VOCs. The burner technology appears to offer an environment resulting in high destruction efficiencies. Analysis of criteria pollutants using a CEM shows low emissions of NO<sub>x</sub>, CO, and HCs.

The unexpected finding of trace amounts (7.01 ng/Nm<sup>3</sup>, corrected to 7% O<sub>2</sub>) of PCDD/PCDFs during the chlorobenzene test seems anomalous, given the thermal environment. However, further work is required to determine the validity of the detection. PIC results showed small (0.2 ppb), but measurable, quantities of chlorinated hydrocarbons in tests with methylene chloride and dichlorobenzene. Analysis of the VOST tubes used for testing is suggested. These results certainly warrant further investigation to determine whether formation is due to the combustion process or sampling train.

### Destruction Efficiency

Based on the evaluation test program results and source tests on the commercial systems described above, the premixed inward-fired radiant thermal oxidizer technology provides DEs of the target compounds tested typically above 99.99 percent, including chlorinated and fluorinated hydrocarbons. Commercial installations using this technology also show DEs above 99.9 percent, consistent with evaluation test program results.

### Suitable Applications

The inward-fired premixed radiant burner technology appears suitable for applications requiring high destruction efficiencies and low criteria pollutant emissions potentially allowing for simplified permitting and higher process throughput. In particular, halogenated-VOC processes would be appropriate users, including pharmaceutical production, metal degreasing, and dry cleaning.

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Table 1. Toxic Air Contaminant Trigger Levels for Bay Area Air Quality Management District

| Compound  | CAS Number | Trigger Level (lb/year)* |
|---|------------|--------------------------|
| Benzene   | 71432      | 6.70E+00                 |
| Carbon tetrachloride  | 56235      | 4.60E+00                 |
| Chlorinated dibenzodioxins and dibenzofurans<br>(TCDD equivalent) | 1746016**  | 1.20E-06                 |
| Chlorobenzene   | 108907     | 1.35E+04                 |
| Chlorofluorocarbons   | **         | 1.353+05                 |
| Dibromo-3-chloropropane,1,2-(DBCP)                                | 96128      | 9.703-02                 |
| Hexachlorobenzene   | 118741     | 3.90E-01                 |
| Methyl chloroform (1,1,1-TCA)                                     | 71556      | 6.18E+04                 |
| Methylene chloride  | 75092      | 1.90E+02                 |
| Perchloroethylene (tetrachloroethylene)                           | 127184     | 3.30E+01                 |
| Trichloroethylene   | 79016      | 9.70E+01                 |
| Xylenes   | 1330207**  | 5.79E+04                 |

\* 1 lb = 0.45 kg

\*\* This is a chemical compound group. If a CAS number is listed, it represents only a single chemical within the chemical class (for metallic compounds, the CAS number of the elemental form is listed; for other compounds, the CAS number of a predominant compound in the group is given).

Table 2. Matrix for Primary Organic Hazardous Constituents Used for Destruction Efficiency Tests

| Test Condition                          | Target Concentration | POHCs (VOST)  | POHCs (Tedlar Bag) | PCDD/PCDF Test |
|---|----------------------|---------------|--------------------|----------------|
| 2-Butanone (MEK)                        | 100 ppm              | 3 x (2 tests) | 0                  | 0              |
| Methylene chloride<br>(Dichloromethane) | 100 ppm              | 3             | 0                  | 0              |
| O-Xylene                                | 30 and 60 ppm        | 3 x (2 tests) | 0                  | 0              |
| Chlorobenzene                           | 100 ppm              | 9             | 0                  | 1              |
| Trichloroethylene                       | 100 and 500 ppm      | 3 x (2 tests) | 0                  | 0              |
| Dichloroethylene                        | 100 ppm              | 3             | 0                  | 0              |
| Dichlorodifluoroethane                  | 100 and 1,000 ppm    | 0             | 3 x (2 tests)      | 0              |
| Hexafluoroethane                        | 100 and 1,000 ppm    | 0             | 3 x (2 tests)      | 0              |
| Field blank                             | N/A                  | 3             | 1                  | 1              |
| Laboratory blank                        | N/A                  | 2             | N/A                | 0              |
| Matrix spikes                           | N/A                  | 2             | 1                  | 0              |

N/A - Not Applicable

Table 3. Destruction Efficiency Results

| POHC or Condition                       | Average Run<br>POHC<br>Concentration<br>(ppm <sub>v</sub> ) | Molecular<br>Weight<br>(g/mole) | Average<br>Destruction<br>Efficiency <sup>*</sup><br>(%) | Minimum<br>Detection<br>(ng/liter) | DRE<br>Detection<br>Limit <sup>**</sup><br>(%) |
|---|---|---------------------------------|--|------------------------------------|--|
| 2-Butanone (MEK)                        | 99  | 72                              | 99.9998  | 0.5                                | 99.999843                                      |
| 2-Butanone (MEK)                        | 92  | 72                              | 99.9988  | 0.5                                | 99.999831                                      |
| Methylene chloride<br>(Dichloromethane) | 97  | 85                              | 99.9766  | 0.5                                | 99.999864                                      |
| O-Xylene                                | 36  | 106                             | 99.9880  | 0.5                                | 99.999706                                      |
| O-Xylene                                | 61  | 106                             | 99.9996  | 0.5                                | 99.999827                                      |
| Chlorobenzene                           | 55  | 12.5                            | 99.9982  | 0.5                                | 99.998371                                      |
| Chlorobenzene                           | 88  | 112.5                           | 99.9998  | 0.5                                | 99.999887                                      |
| Chlorobenzene                           | 92  | 112.5                           | 99.9996  | 0.5                                | 99.999892                                      |
| Trichloroethylene                       | 117   | 131                             | 99.9994  | 0.5                                | 99.999927                                      |
| Trichloroethylene                       | 542   | 131                             | 99.9994  | 0.5                                | 99.999984                                      |
| Dichloroethylene                        | 59  | 97                              | 99.9956  | 0.5                                | 99.999804                                      |
| Dichlorodifluoroethane <sup>***</sup>   | 100   | 102                             | 99.9999  | 0.2                                | 99.999956                                      |
| Dichlorodifluoroethane <sup>***</sup>   | 1,000   | 102                             | 99.9999  | 0.2                                | 99.9999956                                     |
| Hexafluoroethane <sup>***</sup>         | 100   | 138                             | 99.9999  | 0.2                                | 99.999967                                      |
| Hexafluoroethane <sup>***</sup>         | 1,000   | 138                             | 99.9999  | 0.2                                | 99.9999967                                     |
| Combustion blank                        | 0   | N/A                             | N/A  | 0.5                                | N/A  |

\* Not corrected for combustion blanks.

\*\* DRE D.L. (%) =  $\{[\text{POHC}_{\text{in(ppm)}} - ((10\text{ng}/20\text{L}) * (1\text{g}/1\text{EQng}) * (1\text{mol}/\text{MW}_{\text{g}}) * (22.42/\text{mol}) * 1.0\text{E}6)_{\text{(ppm)}}] / \text{POHC}_{\text{in(ppm)}}\} * 100$

\*\*\* DREs for these tests were calculated using a PQL of 0.2ng on the column (the lowest level seen in static bulb calibrations) for the 1L injections.

Table 4. Criteria Pollutant Emissions

| POHC                                    | NO <sub>x</sub><br>(ppm <sub>v</sub> ) | CO<br>(ppm <sub>v</sub> ) | HCS<br>(ppm <sub>v</sub> ) | POHC                   | NO <sub>x</sub><br>(ppm <sub>v</sub> ) | CO<br>(ppm <sub>v</sub> ) | HCS<br>(ppm <sub>v</sub> ) |
|---|--|---------------------------|----------------------------|------------------------|--|---------------------------|----------------------------|
| 2-Butanone (MEK)                        | 2.23                                   | -1.71                     | -7.52                      | Trichloroethylene      | 1.14                                   | 0.02                      | -5.22                      |
| 2-Butanone (MEK)                        | 2.46                                   | -0.12                     | -4.63                      | Trichloroethylene      | 1.55                                   | -0.41                     | -0.82                      |
| Methylene chloride<br>(Dichloromethane) | -0.12                                  | 0.61                      | -2.13                      | Dichloroethylene       | 1.66                                   | -0.84                     | -6.94                      |
| O-Xylene                                | 1.71                                   | -0.59                     | -5.97                      | Dichlorodifluoroethane | 2.03                                   | -0.37                     | -1.27                      |
| O-Xylene                                | 1.99                                   | 1.40                      | -1.37                      | Dichlorodifluoroethane | 2.00                                   | -1.87                     | 0.14                       |
| Chlorobenzene                           | 1.20                                   | -0.37                     | -2.81                      | Hexafluoroethane       | 1.54                                   | -1.99                     | -0.86                      |
| Chlorobenzene                           | 1.70                                   | 0.26                      | -7.23                      | Hexafluoroethane       | 1.84                                   | -0.01                     | 2.80                       |
| Chlorobenzene                           | 2.10                                   | -1.37                     | -6.37                      | Combustion blank       | 2.48                                   | 0.15                      | -5.32                      |

\* As measured (wet at approximately 10% O<sub>2</sub>), average of test condition.

\*\* Measurements based on propane.

Table 5. PCDD/PCDF Results from Chlorobenzene Test

| Congener    | Lab Blank<br>(ng) | Sample<br>(ng) | Field Blank<br>(ng) |
|-------------|-------------------|----------------|---------------------|
| Total TCDD  | (0.007)           | 0.85           | 1.1                 |
| Total PeCDD | 0.02              | 0.78           | (0.01)              |
| Total HxCDD | 0.07              | 1.0            | 0.03                |
| Total HpCDD | 0.03              | 7              | 0.07                |
| Total TCDF  | (0.006)           | 4.3            | (0.008)             |
| Total PeCDF | 0.05              | 3.3            | 0.03                |
| Total HxCDF | 0.09              | 3.3            | 0.14                |
| Total HpCDF | 0.06              | 2.5            | 0.14                |

( ) Detection limit

Table 6. Destruction Efficiencies for 10,000-CFM EDGE PLUS<sup>+</sup> QR System

| Condition                                 | Average         |                     |                      |
|---|-----------------|---------------------|----------------------|
|   | System Inlet    | Concentrator Outlet | Oxidizer Outlet      |
| Test Location                             |                 |                     |                      |
| Oxidizer temperature, °C (°F)             | N.A.            | N.A.                | 788°C (1,450)        |
| Flowrate, L/min (dscfm)                   | 278,345 (9,828) | 293,639 (10,368)    | 30,446 (1,075)       |
| Stack temperature                         | 18°C (65)       | 26°C (79)           | 35°C (95)            |
| H <sub>2</sub> O, %                       | 1.2             | 0.9                 | 7.7                  |
| O <sub>2</sub> , %                        | 20.9            | 20.9                | 9.7                  |
| CO <sub>2</sub> , ppm <sub>v</sub> or (%) | 395             | (0.04)              | (6.5)                |
| CH <sub>4</sub> , ppm <sub>v</sub>        | 1.1             | N.M.                | N.M.                 |
| THC, ppm <sub>v</sub>                     | N.A.            | 20.0                | 2.1                  |
| TOC, ppm <sub>v</sub>                     | 686             | N.A.                | N.A.                 |
| TNMHC, ppm <sub>v</sub>                   | 274             | 3.9                 | 1.1                  |
| TNMHC, lbs/hr (kg/hr) as CH <sub>4</sub>  | 6.71 (3.02)     | 0.102 (0.046)       | 0.003 (0.0014)       |
| TNMHC D.E., %                             |                 | 98.38 (combined)    | 99.2 (oxidizer only) |

N.A. Not Applicable

N.M. Not Measured

Table 7. Emission Measurements for 100-CFM EDGE QR Thermal Oxidizer for Soil Remediation

| Location<br>Compound                | Inlet Concentration (ppm <sub>v</sub> ) | Exhaust Concentration (ppm <sub>v</sub> ) |
|-------------------------------------|---|---|
| Benzene                             | 21.3                                    | <0.05                                     |
| Toluene                             | 73.8                                    | <0.05                                     |
| Ethylbenzene                        | 9.5                                     | <0.05                                     |
| M&P Xylene                          | 36.7                                    | <0.05                                     |
| O-Xylene                            | 15.9                                    | <0.05                                     |
| <b>Total Petroleum Hydrocarbons</b> | <b>457</b>                              | <b>&lt;0.05</b>                           |

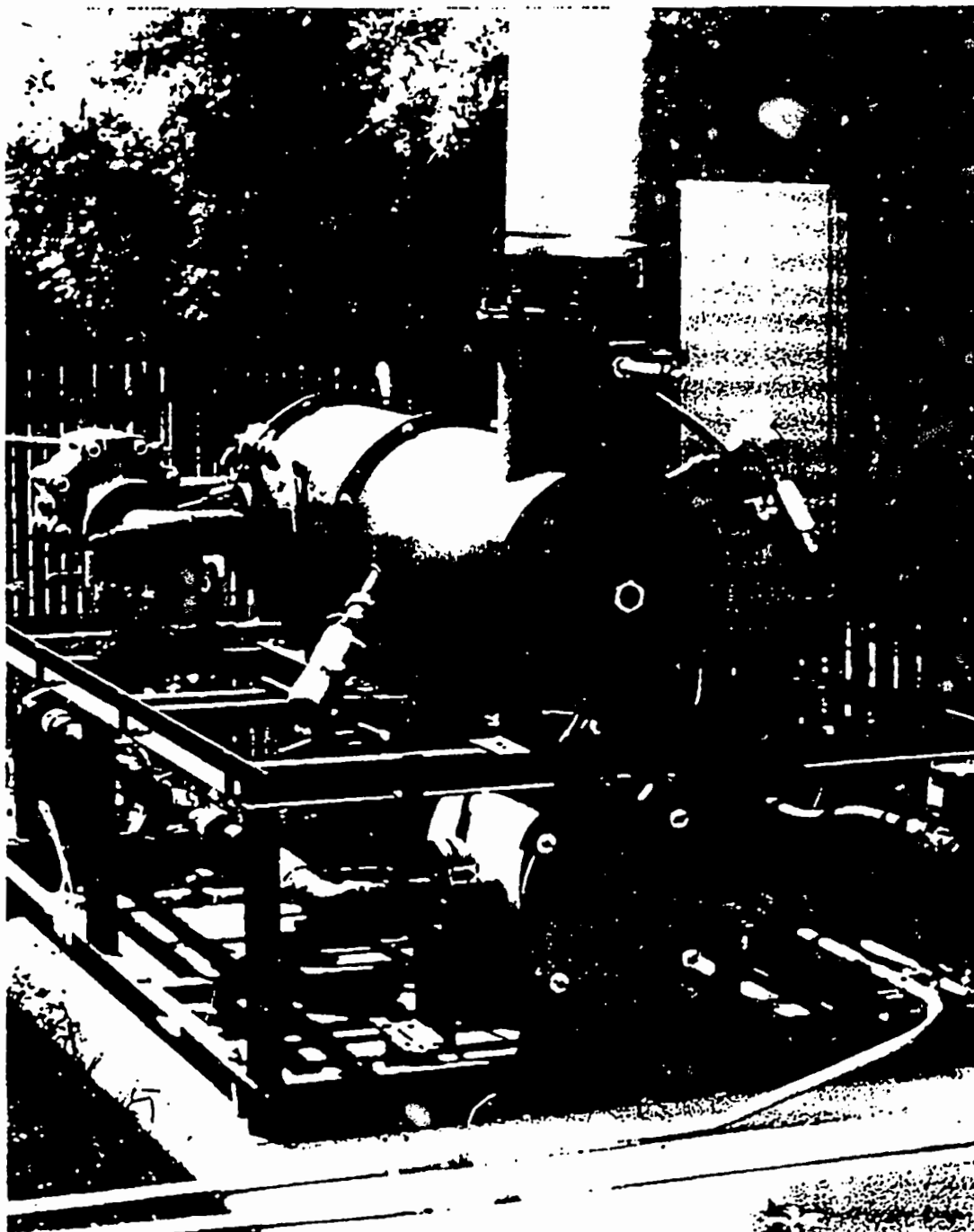


Figure 1. 100-CFM Inward-Fired Thermal Oxidizer for VOC Destruction Testing at EPA

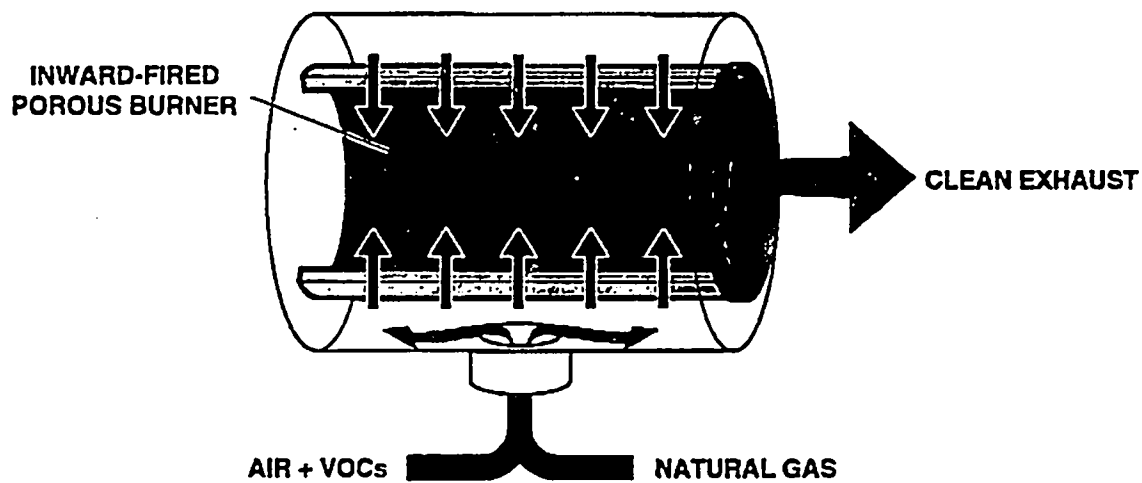


Figure 2. Premixed Inward-Fired Surface Combustion Radiant Burner

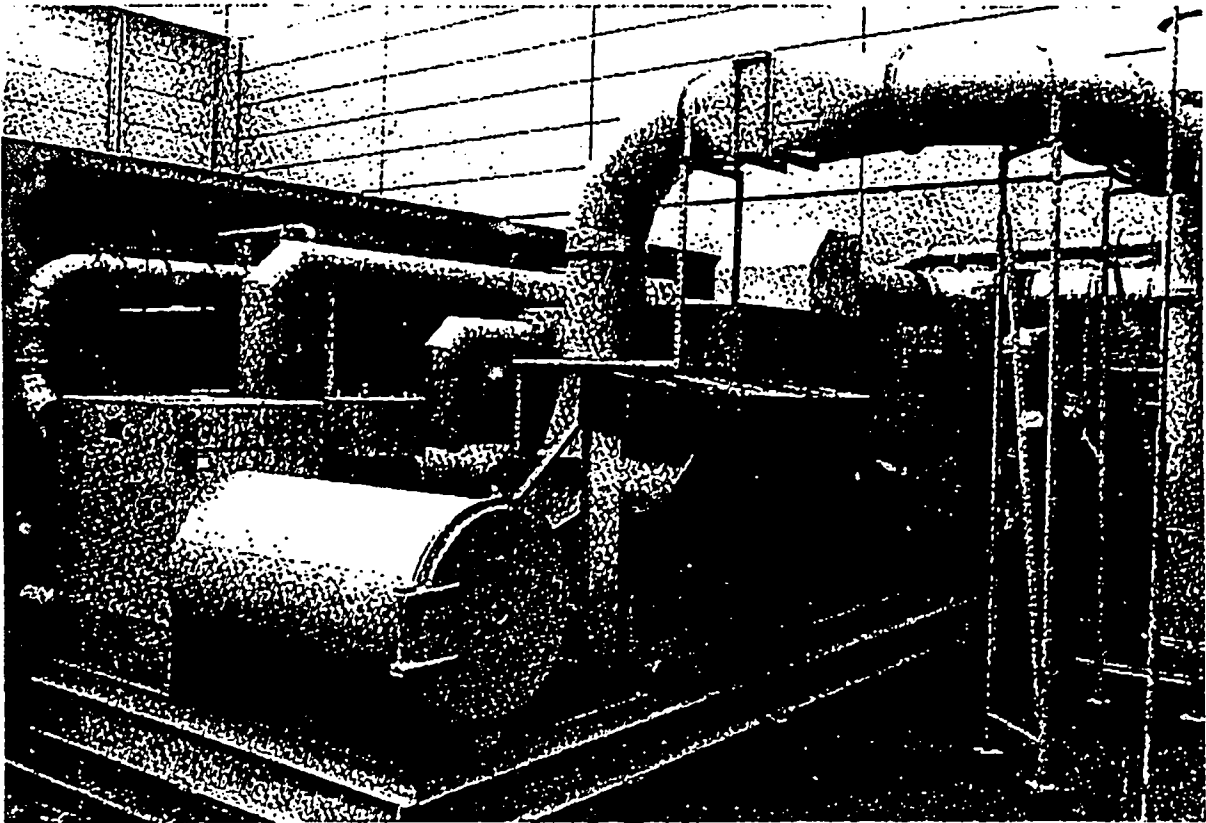


Figure 3. 10,000-CFM EDGE PLUS<sup>+</sup> QR Thermal Oxidizer

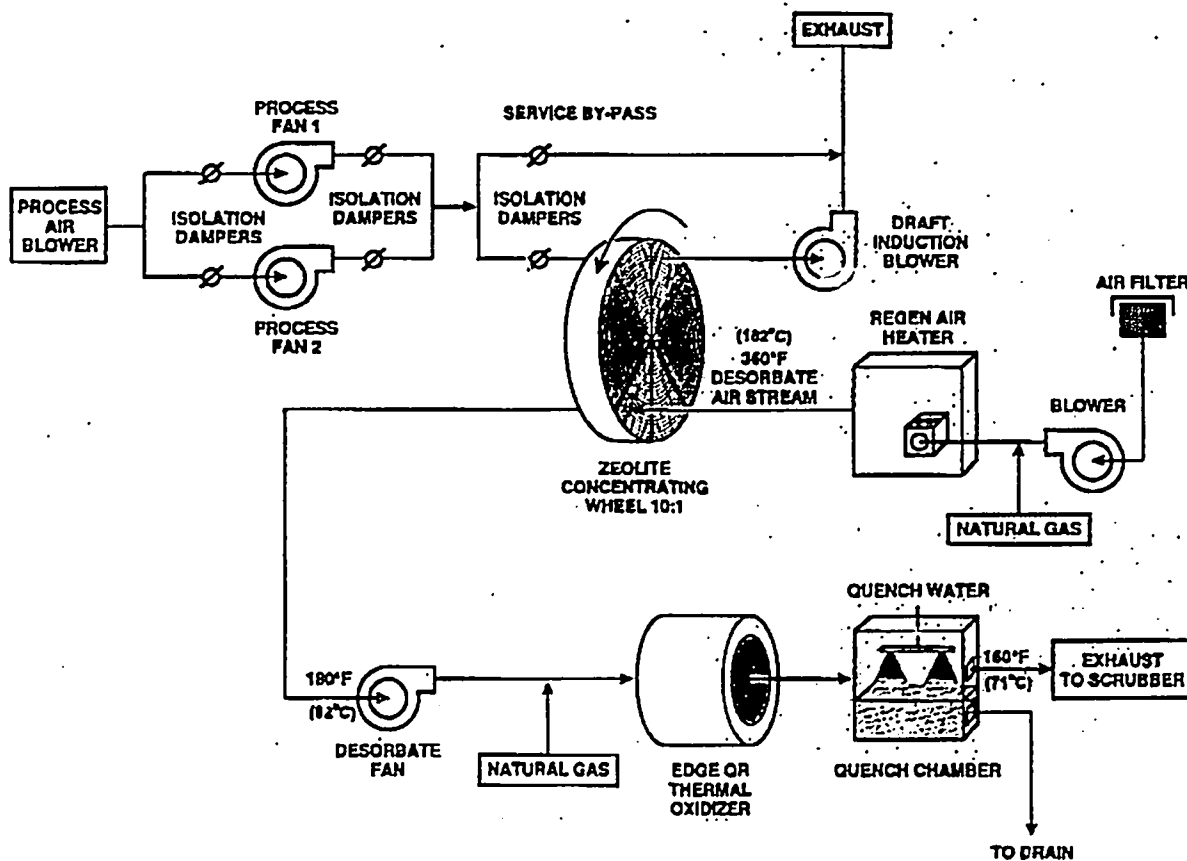


Figure 4. Process Diagram for 10,000-CFM EDGE PLUS+ QR



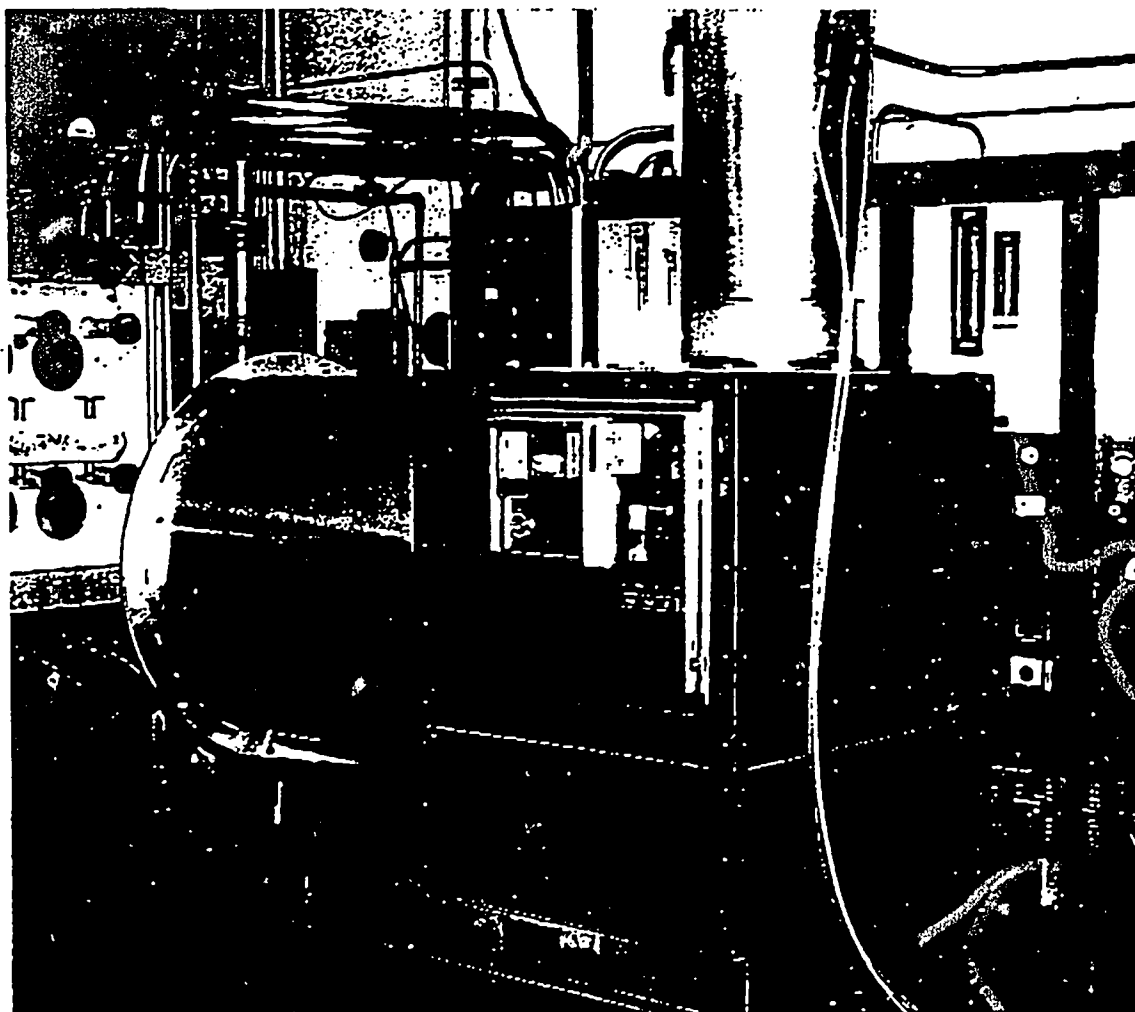


Figure 5. 500-CFM EDGE QR Thermal Oxidizer

| NRMRL-RTP-P-091 <span style="float: right;">TECHNICAL REPORT DATA<br/><i>(Please read Instructions on the reverse before completing)</i></span>   |  |  |
|---|--|--|
| 1. REPORT NO.<br><b>EPA/600/A-96/033</b>  | 2.   | 3. REI   |
| 4. TITLE AND SUBTITLE<br><b>Destruction of Halogenated VOCs Using Premixed Radiant Burner</b>   |  | 5. REPORT DATE   |
|   |  | 6. PERFORMING ORGANIZATION CODE                                  |
| 7. AUTHOR(S) <b>D. F. Bartz, B. N. Marshall (Alzeta); K. Bruce, A. Lombardo (Acurex); and C. W. Lee (EPA)</b>   |  | 8. PERFORMING ORGANIZATION REPORT NO.<br><b>ES96-35</b>          |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br><b>Alzeta Corporation Acurex Environmental Corp.<br/>2343 Calle del Mundo 4915 Prospectus Dr.<br/>Santa Clara, CA Research Triangle Park, NC<br/>95054 27709</b>   |  | 10. PROGRAM ELEMENT NO.  |
|   |  | 11. CONTRACT/GRANT NO.<br><b>NA (Inhouse)</b>                    |
| 12. SPONSORING AGENCY NAME AND ADDRESS<br><b>EPA, Office of Research and Development<br/>Air Pollution Prevention and Control Division<br/>Research Triangle Park, NC 27711</b>   |  | 13. TYPE OF REPORT AND PERIOD COVERED<br><b>Published paper:</b> |
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| 15. SUPPLEMENTARY NOTES <b>APPCD project officer is C. W. Lee, Mail Drop 65, 919/541-7663. Presented at AWMA Specialty Conference, Emerging Solution to VOC and Air Toxics Control, Clearwater, FL, 2/28-3/1/96.</b>  |  |  |
| 16. ABSTRACT <b>The paper describes the destruction of halogenated volatile organic compounds (VOCs) using a premixed radiant burner. Alzeta Corporation has developed a natural-gas-fired thermal oxidizer to provide emission control for industrial exhaust streams where stringent emission limits of VOCs are required. Measurements, made with assistance of the U. S. EPA at Research Triangle Park, NC, show destruction efficiencies (DEs) between 99.9766 and 99.999% for eight common halogenated compounds. This thermal oxidizer technology utilizes an inward-fired premixed radiant burner that operates at high levels of excess air (typically 80 to 100%) to achieve nitrogen oxide (NOx) and carbon monoxide (CO) emissions below 10 ppmv, corrected to 3% oxygen (O2). A brief discussion of pertinent regulations and emissions of concern is presented. The EPA test program is presented with results. Three similarly designed commercial thermal oxidizers are described, including emission test results.</b> |  |  |
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| a. DESCRIPTORS  | b. IDENTIFIERS/OPEN ENDED TERMS  | c. COSATI Field/Group  |
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