

Assessment of a new carbon tetrachloride destruction system based on a microwave plasma torch operating at atmospheric pressure

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Abstract

A new system for destroying volatile organic waste based on a microwave plasma torch that operates at atmospheric pressure and is coupled to a reactor affording isolation of output gases and adjustment of the plasma discharge atmosphere is proposed. The system was assessed by using carbon tetrachloride as the target volatile organic compound (VOC) and argon as the main gas in a helium atmosphere. Under optimal conditions, a microwave power of less than 1000 W was found to reduce the CCl₄ concentration at the reactor outlet to the parts-per-billion level and hence to virtually completely destroy the VOC. With high argon flow-rates and CCl₄ concentrations, the energy efficiency can reach levels in excess of 3000 g/kWh. Output gases and species in the plasma, which were identified by gas chromatography and light emission spectroscopy, respectively, were found to include no halogen-containing derivatives resulting from the potential cleavage of CCl₄. In fact, the main gaseous byproducts obtained were CO₂, NO and N₂O, in addition to small traces of Cl₂, and the solid byproducts Cl₂Cu and various derivatives depending on the particular reactor zone.

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1. Introduction

The processes involved in the manufacturing and transformation of a wide variety of products including silicones, tyres, paints, dyes, detergents, fire-proof materials and semiconductors produce undesirable waste that is disposed of by dumping in depots or discharge into the aquatic medium or the atmosphere. This has resulted in increasing contamination of ground waters and degradation of tropospheric ozone. Chlorinated volatile organic compounds (VOCs) such as trichloroethylene (TCE) and carbon tetrachloride (CTC) are massively used industrially on the grounds of their rapid evaporation, low flammability and reactivity, and ability to expeditiously dissolve a wide range of organic substances with a high efficiency. Hence their widespread use in vapour degreasing, metal cleaning and dry cleaning processes [1]. Because of their ready evaporation, VOCs reach the air very easily, and also soil and ground water,

thereby posing health hazards and requiring complex, costly remediation [2,3]. A number of technologies for destroying VOCs have so far been tested including thermal decomposition [4], catalytic oxidation [5], biofiltration, carbon adsorption, membrane separation, UV oxidation [6], condensation and plasma-based procedures [7].

Plasma-based technologies have steadily grown in use for the suppression of environmental hazards ranging from air pollutants to solid wastes. As with ashing, the destructive efficiency of thermal plasmas relies on the use of high enough temperatures to break bonds in organic species in order to generate and facilitate the propagation of free radicals [8].

Non-thermal plasmas provide an alternative method for generating highly reactive species; electrons are accelerated by the applied electrical fields and transfer their energy via elastic and non-elastic collisions with neutral molecules. The reactions occurring under these conditions are usually far from thermodynamic equilibrium and result in kinetic rates of destruction associated with electron temperatures of 10 000–20 000 K; by contrast, the neutral gas remains at much lower temperatures. This mechanism uses most of the applied energy to generate

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radicals and excited atomic and molecular species, thereby facilitating the decomposition of contaminant molecules. Although the temperature of a non-thermal plasma is not so highly influential on the destruction efficiency, an increased temperature facilitates the process. In addition to enhanced destruction and removal, plasma-based chemical processes provide some advantages such as low implementation, operating and capital costs, and modest facility size requirements, in relation to conventional VOC destruction techniques.

The proposed VOC destruction system is based on the axial injection torch (Torche a Injection Axiale, TIA) developed by Moisan et al. in 1994 [9]. The resulting plasma provides an appropriate energetic environment for destroying waste and is highly stable against impedance changes caused by the insertion of molecular gases or organic compounds. The microwave plasma obtained at atmospheric pressure never reaches thermodynamic equilibrium between neutral species, ions and electrons. Also, it possesses some typical properties of non-thermal plasmas including a high electron kinetic temperature (8000 K in argon plasma) [10] which facilitates the fragmentation of contaminant molecules and formation of chemically reactive radicals via collisions; also, it has a relatively high heavy particle temperature (2500 K in argon plasma), which is not decisive but facilitates the destruction of compounds.

This fact is the one that makes to this plasma introduce newness with respect to the use other non-thermal plasmas, such as corona, dielectric barrier discharges (DBD), surface discharge for the destruction of carbon tetrachloride. The high temperature of neutral gas allows to destroy higher concentrations of VOCs, in the range of 10^5 ppmv, with efficiencies of 99.99%. Urashima and Chang [11] compare the application range of different technologies for the removal of VOC and conclude that the maximum value of introduced concentration in a non-thermal plasma is around 10^4 ppmv, and in thermal plasma is around 10^5 ppmv. This get together the high values of gas flow that is

possible to reach, over 20 L/min, makes a device very promising in industrial applications in which it is needed to destroy great amount of VOCs in the shortest possible time.

The axial injection torch is a very versatile device that is possible to use with different main gases, for example helium, argon, hydrogen, nitrogen or even air. This work studies the percentage of destruction with argon plasma that is shown better results than other gases: higher energetic efficiency, better destruction and removal efficiency (%DRE), and less final byproducts. Also this plasma is well know because it has been characterized in depth in the literature and by our research group (temperatures, densities, etc.) [12,13] and it is possible to predict the behaviour of the plasma with the introduction of volatile organic compounds.

2. Experimental

The proposed experimental set-up for waste destruction and byproduct analysis consists of three distinct parts, namely: (a) the destruction zone, which includes a microwave plasma torch operating at atmospheric pressure and a reactor intended to control the discharge atmosphere and output gases; (b) a unit for inserting liquid and gaseous samples, which ensures industrial utility of the system; and (c) the detectors and analytical systems required to precisely determine the resulting solid and gaseous byproducts.

Fig. 1 depicts the proposed VOC destroying system and Table 1 describes its components.

2.1. Microwave generator and its associated reactor

The plasma torch consists of a microwave transmission area and a plasma generation area. The former comprises a tubular waveguide connected to a rectangular waveguide (WR340). The resonant microwave is adjusted by sliding short circuits and is induced into a copper antenna located at the centre of the reaction

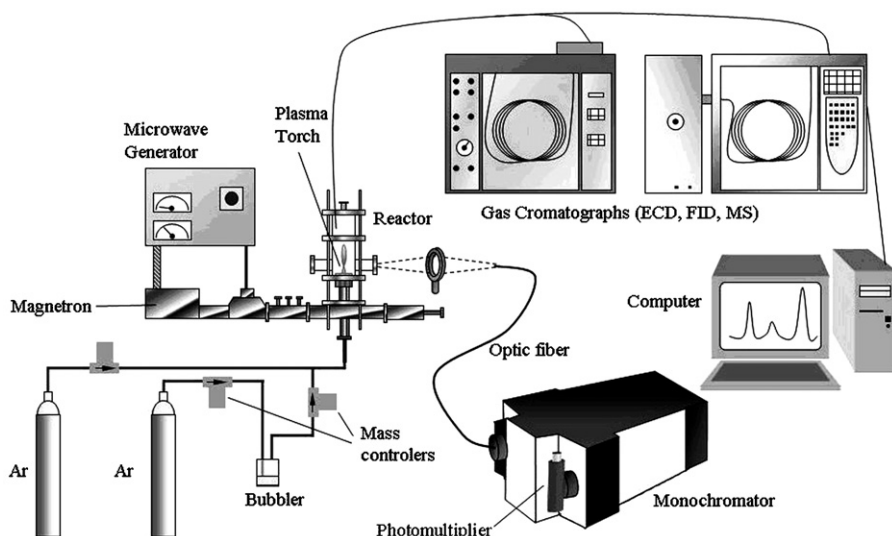


Fig. 1. Schematic diagram of the proposed VOC destruction set-up.

Table 1
Instrumental components of the proposed CCl₄ destruction system

Component	Description
Microwave generator	MW-GIRE3328-3K0-006 (MUEGGE) at 2.45 GHz
Microwave launcher	TIA (Montreal University)
Reactor	Spanish patent [11]
CCl ₄ source	Panreac (99%)
Gas chromatograph	AGILENT 4890D Column: HP-5, 15 m, 0.53 mm i.d., 1.5 μm film thickness Injection method: 6-way valve Detectors: FID and ECD
GC/MS	THERMO FINNIGAN TRACE DSQ Column: DB-1, 60 m, 0.32 mm i.d., 5 μm film thickness Injection method: 6-way valve Detector: Quadrupole Mass Spectrometer Siemens D5000
X-ray diffraction spectrometer	Cu Kα, 40 kV, 30 mA Electron microprobe: JEOL JSM-6300 X-ray detector: ATW2-6699 (Oxford Instruments) HR-460 (Jovin-Yvon)
Monochromator	Grating: 1200 grooves mm ⁻¹ Computer-controlled Spectralink system
Flow controller	Mass flow controllers: FC280 Control system: Dynamass (Tylan General)

section, through which the main gas containing the contaminants is circulated. This area is coupled to the reactor patented by our group [14], and a detail of this reactor is shown in Fig. 2. The antenna tip is extended into the reaction chamber of the plasma reactor, which constitutes the lower section and is fitted with two windows intended to facilitate spectroscopic analyses. The recombination chamber, which constitutes the upper section, is furnished with a central hole for evacuating output gases and two additional holes for collection of gas samples from the reactor.

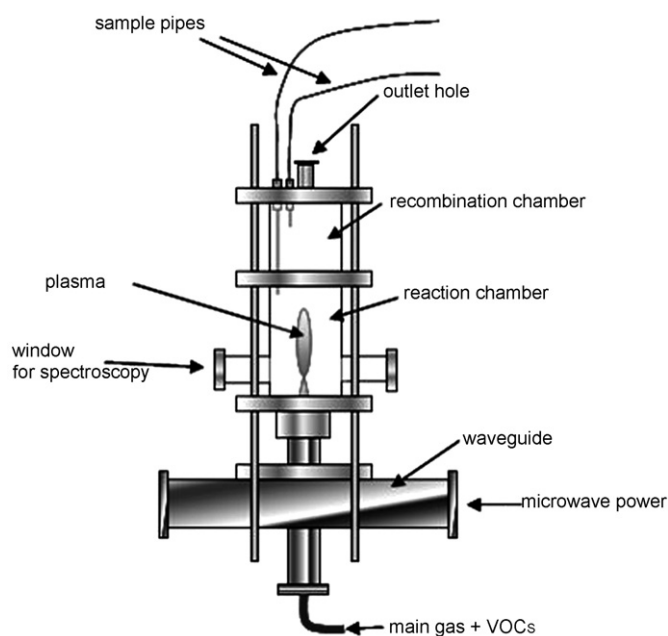


Fig. 2. Schematic diagram of the plasma reactor (Spanish patent no. P200201328).

Using a reactor coupled to the plasma device has the advantages that it allows any contaminants inserted to be isolated, increases the stability of the plasma and improves coupling of the microwave energy supplied. Also, the reactor allows the inner atmosphere used to discharge the plasma to be adjusted, thereby facilitating control of the production of intermediate products. In this work, we used an outer atmosphere consisting of helium, an inert gas with a higher ionization potential than argon, in order to ensure stability in the plasma. The use of a waveguide, and the fact that the plasma was allowed to freely expand in such an atmosphere, avoided the power restrictions imposed by a coaxial power cable or encapsulation of the plasma within a quartz tube. This facilitates the use of a variety of gases including helium – which possesses a high ionization energy – argon or air to generate the plasma.

2.2. Sample insertion

The target VOC was liquid carbon tetrachloride 99.99% pure that was inserted in vapour form by bubbling [15] the main gas, argon, through it. The gas left the bubbler saturated with CCl₄, which resulted in the presence of high concentrations of the contaminant depending on the particular temperature and vapour pressure of the VOC.

The saturated gas was mixed with pure argon in the desired proportion. Clean and contaminated gas were mixed via a T-piece the two branches of which were fitted to mass flow controllers in order to adjust the flow-rate as required. The final contaminant concentration in the mixture was confirmed by gas chromatography and found to depart by less than 1% from target in all instances. This mixing system allows the output concentration to be readjusted in response to a change in either flow-rate within one minute and affords a wide range of contaminant concentrations (5–12 000 ppm).

2.3. Analytical techniques

We analysed gaseous byproducts, solid deposits and various species present in the plasma. The gaseous byproducts were separated and analysed by gas chromatography on an Agilent 4890D instrument equipped with an electron capture detector (ECD) and a flame ionization detector (FID) that were coupled to it in parallel via a Y splitter (50/50). The chromatograph was furnished with an HP-5 fused silica capillary column (15 m × 0.53 mm i.d., 1.5 μm film thickness) and a split/splitless injector for capillary columns. Mass spectroscopy (MS) analyses were conducted on a Thermo Finnigan Trace GC gas chromatograph equipped with a split/splitless injector and a DB-1 fused silica capillary column (60 m × 0.32 mm i.d., 5 μm film thickness). The chromatograph was coupled to a Thermo Finnigan Trace DSQ mass spectrometer equipped with an electron impact (EI) ionization source of 70 eV and a quadrupole mass filter. This system can be used in the complete spectrum (SCAN) and selected ion monitoring (SIM) modes. The mass spectrometer was calibrated on a daily basis prior to byproduct analysis, using perfluorotributylamine (PFTBA) as standard.

Gaseous samples were inserted into the gas chromatographs via two VALCO 6-way valves furnished with a 250 μL loop that was filled with gas from the reactor and inserted into the chromatographic column by means of the split/splitless injector. Gas samples were collected at various points within the reactor and transferred to the entry loop of the chromatographs using an SKC extraction pump at a constant flow-rate of 25 mL/min. This injection method results in substantially reduced systematic errors arising from the injection of liquids, thereby improving reproducibility.

Solid deposits on the reactor glass and metal disks were analysed by X-ray diffraction spectroscopy, using a Siemens D500 instrument with Cu K α radiation at 40 kV at 30 mA. All diffraction patterns were obtained by scanning the goniometer from 5° to 90° (2 θ) at a rate of 0.05° s⁻¹. The electron microprobe technique was implemented on a JEOL JSM-6300 scanning electron microscope using an acceleration voltage of 20 kV and a working distance of 15 mm. The X-ray detector was an ATW2-6699 model from Oxford Instruments.

The analysis of the species present in the plasma during the destruction of CCl₄ was consistent with the gaseous byproducts and deposited solids identified, and suggested new pathways for the loss of chloride and carbon in the reaction with copper at the coupler tip. This analysis, which was done spectroscopically, required altering the Pyrex tube in the reaction chamber of the reactor with respect to the original patent [14] in order to open two flat windows for precise focusing of light from the most intense zone in the plasma onto a lens that in turn focused it on an optical fibre (see Fig. 1), the fibre transferring the light beam to a Jobin-Yvon HR460 monochromator with a diffraction grating of 1200 lines/mm. A photomultiplier was coupled at the monochromator outlet in order to integrate the light output, which was monitored by a computer furnished with a Jobin-Yvon DataScan2 controller.

3. Results

3.1. Destruction of carbon tetrachloride

The CCl₄ destruction method was optimized by using an argon plasma under the most suitable conditions regarding microwave power, gas flow-rate, coupler tip outlet cross-sectional area and CCl₄ concentration. For each set of experimental conditions, we determined the CCl₄ concentration at the reactor outlet by gas chromatography. Such a concentration was a result of the amount of carbon tetrachloride initially fed into the main gas, which was also determined by GC, being destroyed into the plasma.

3.1.1. Influence of microwave power

The principal mechanism for the decomposition of contaminant molecules in a non-thermal plasma is via electron collisions. The efficiency of such collisions increases with increase in the amount of energy released to free electrons in the plasma. Therefore, the efficiency with which contaminants can be destroyed will depend directly on the plasma density and electron temperature.

The microwave power supplied to the plasma torch via the waveguide has a direct effect as it raises and maintains the electron temperature of the plasma [12]; therefore, increasing the amount of power supplied will result in improved destruction of the compound introduced into the main gas flow.

Fig. 3 shows the variation of the carbon tetrachloride concentration at the reactor outlet as a function of the supplied microwave power. The argon plasma was fed with a 1000 ppm concentration of CCl₄ and the flow-rate kept constant at 1.0 L/min. At a microwave power settings from 300 to 800 W, the CCl₄ output concentration decreased – and the contaminant destruction efficiency increased – with increasing power. No substantial improvement was observed above 900 W, however, as the contaminant output concentration was virtually the same as that obtained at 800 W (viz. in the parts-per-trillion region). Therefore, carbon tetrachloride at these concentration levels can

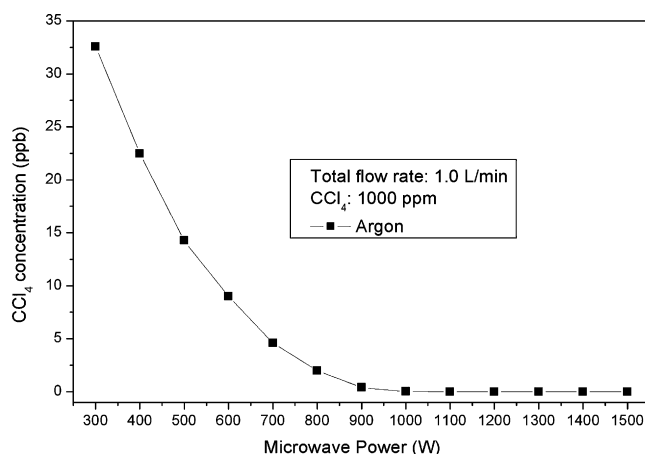


Fig. 3. Variation of the CCl₄ concentration in the argon plasma as a function of the microwave power applied.

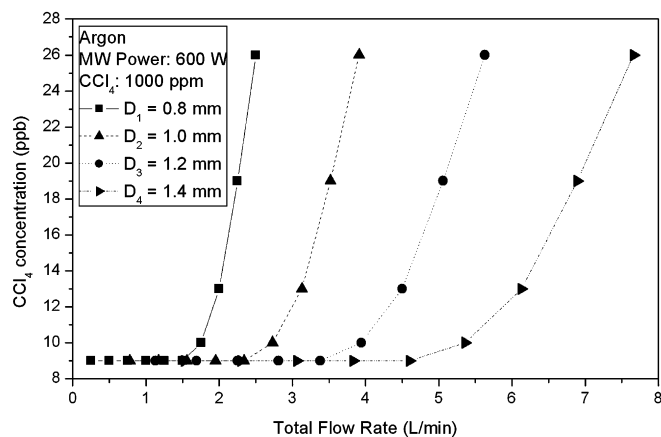


Fig. 4. Variation of the CCl_4 concentration in the argon plasma as a function of the total flow-rate (argon plus CCl_4) at different inner diameters of the coupler tip.

be easily destroyed on an industrial scale by using a moderate microwave power.

3.1.2. Influence of the flow-rate

We examined the effect of changes in flow-rate in the mixture of inert gas and vaporized waste at a constant concentration of the latter on the CCl_4 destruction efficiency. Fig. 4 shows the variation of the CCl_4 concentration at the reactor outlet during the destruction of 1000 ppm carbon tetrachloride in an argon plasma as a function of the total flow-rate of gas at a constant power of 600 W at four different coupler tip inner diameters (viz. 0.8, 1.0, 1.2 and 1.4 mm). As can be seen in the results of 0.8 mm inner diameter, the destruction efficiency was virtually constant at low flow-rates, with CCl_4 output concentrations of ca. 0.9 ppb. Higher flow-rates, however, raised such a concentration and decreased the efficiency as a result. Thus, flow-rates above 1.75 L/min decreased the residence time and led to a poor destruction efficiency, for a inner diameter of 0.8 mm.

Because the diameter of the plasma torch nozzle was kept constant, increasing the flow-rate of gas increased its linear outgoing velocity; therefore, the variable actually affecting the residence time was such a velocity. With an inner diameter of 0.8 mm, the optimum velocity was 30–70 m/s, which corresponded to a flow-rate of 0.6–1.5 L/min irrespective of the microwave power used.

As can be seen in Fig. 4, the variation was similar at all diameters, but shifted to higher flow-rates at the larger ones. As can be seen, gas velocity values within the optimum range allow one to select the flow-rate needed depending on the particular technical and energy efficiency requirements.

3.1.3. Energy efficiency

The energy efficiency, μ , is defined as the amount of waste destroyed per unit energy used in the process; as such, it is a measure of industrial and economic efficiency. The efficiency is expressed in g/kWh units and calculated from (1):

$$\mu = \frac{W_{\text{in}} - W_{\text{out}}}{P} \quad (1)$$

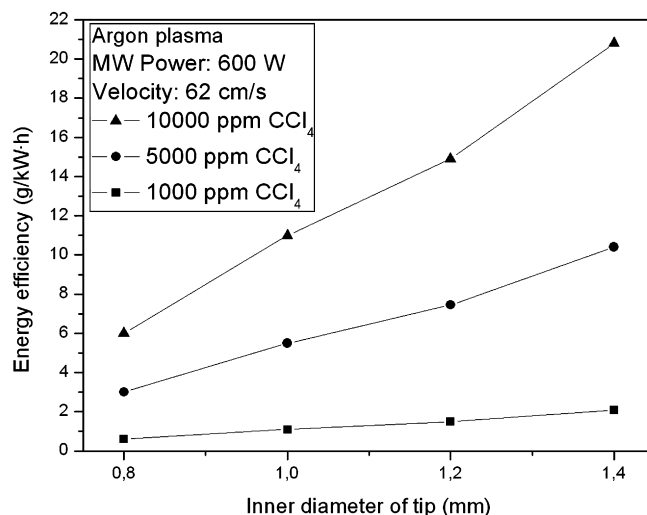


Fig. 5. Variation of the energy efficiency with the inner diameter of the coupler tip.

In Eq. (1) W_{in} and W_{out} denote the incoming and outgoing mass of CCl_4 , respectively, and P is the microwave power used in the destruction process, the former two parameters being calculated from the flow-rate of gas and the measured concentration.

The efficiency of the proposed waste destruction method relies on the practical removal of a large amount of contaminant per unit time by using as little energy as possible. The efficiency can be improved simply by simultaneously increasing the flow-rate of the outgoing gas and the inner cross-sectional area of the coupler tip while keeping the outgoing velocity within the optimum range. This allows efficiency levels close to 3000 g/kWh to be reached for CCl_4 concentrations in the region of 20% by using a coupler tip inner diameter of 1.4 mm, a flow-rate above 10 L/min and a microwave power of 300 W.

Fig. 5 shows the variation of the energy efficiency of an argon plasma containing 1000, 5000 and 10 000 ppm CCl_4 as a function of the inner diameter of the coupler tip. As can be seen, the efficiency increases with increasing diameter of the gas outlet at a constant outgoing velocity. This increases the flexibility of the system as it allows the energy efficiency to be raised simply by using a larger coupler tip diameter and a higher flow-rate of gas.

3.1.4. Influence of the contaminant concentration

Fig. 6 shows the variation of %DRE and the variation of the CCl_4 concentration at the reactor outlet as a function of that fed into the argon plasma at six different microwave power levels, namely: 100, 200, 250, 300, 600 and 1000 W. At a low power levels, the contaminant concentration at the reactor outlet increases with increasing concentration introduced in the plasma; above 300 W, however, the supplied energy suffices to maintain a virtually zero output concentration. In any case, the increase in output concentration with increase in the amount of CCl_4 present in the plasma provides no measure of the destructive efficiency of the plasma as it implies the processing of an increased amount of contaminant per time unit. To this end, one should use the percent

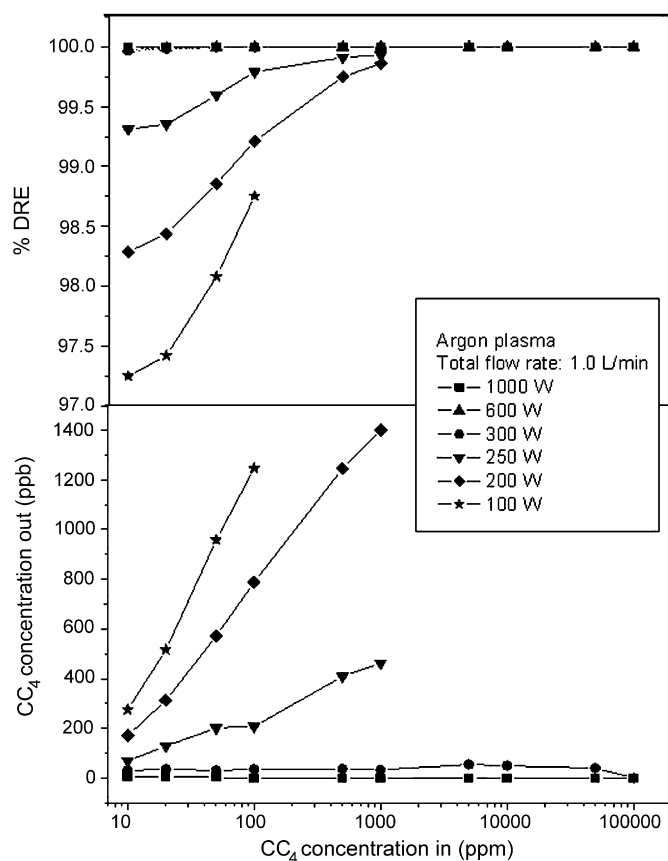


Fig. 6. Variation of %DRE and the CCl_4 concentration at the reactor outlet as a function of that introduced in the plasma at different microwave power levels. The total flow-rate included those of argon and CCl_4 vapour.

destruction and removal of CCl_4 , %DRE, as calculated from the expression (2) [16]:

$$\% \text{DRE} = \left(\frac{W_{\text{in}} - W_{\text{out}}}{W_{\text{in}}} \right) \times 100 \quad (2)$$

where W_{in} is the mass of waste inserted and W_{out} that remaining after the plasma treatment.

As can be seen in Fig. 6, %DRE increases with increasing initial concentration of CCl_4 , which was not apparent from the variation of the CCl_4 concentration at the reactor outlet. A similar result was previously obtained by Yamamoto and Futamura [17] that can be ascribed to the presence of a secondary destruction pathway involving collisions between chlorine and copper radicals formed in fragmentation reactions preceding the destruction of contaminant molecules [18]. Our results are consistent with this assumption but cannot be used to confirm it beyond doubt in the absence of spectroscopic data for the destruction of the plasma itself.

3.2. Analysis of byproducts and species in the plasma

A preliminary study of the byproducts formed during and after the destruction of carbon tetrachloride in the argon plasma was conducted by using four analytical techniques, namely: gas chromatography/mass spectrometry (GC/MS), gas chromatog-

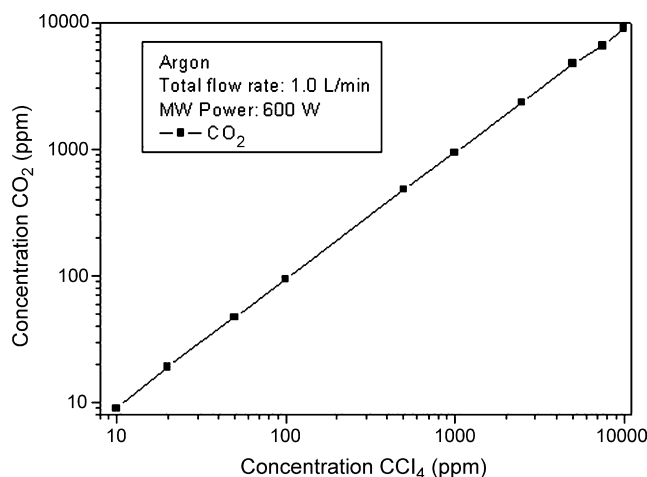


Fig. 7. CO_2 concentration at the reactor outlet vs. CCl_4 concentration introduced (the CO_2 concentration from the air has been subtracted).

raphy with electron capture detection (ECD), X-ray diffraction spectroscopy and light emission spectroscopy.

3.2.1. Gaseous byproducts

The analysis of the byproducts of the destruction of carbon tetrachloride by GC/MS and ECD revealed the presence of no other halogen-containing organic compound than CCl_4 itself [19]; also, under optimal conditions, its concentration never exceeded 10 ppb. In fact, the sole additional species found was Cl_2 [20], which was detected by GC/MS and in very small (trace) amounts. Therefore, alternative pathways for the loss of carbon and chloride in the destruction of CCl_4 must exist.

GC/MS analyses revealed the presence of byproducts including CO_2 [21], NO [22] and N_2O [23]. In support of the carbon balance, shown in the lineal behaviour of Fig. 7, we do not detect any other carbon containing compounds, than CO_2 and CCl_4 , reason why the formation of CO_2 should be the main pathway for the loss of atomic carbon from fragmented CCl_4 , its concentration increasing with increase in that of CCl_4 introduced into the plasma (Fig. 7). However, the variation of the CO_2 concentration at the reactor outlet as a function of the microwave power and of the gas flow is not representative, due to the variation of the CCl_4 destroyed with these parameters is in the range of ppbv (virtually completely eliminated) versus the total concentration of CO_2 , in the range of ppmv. The oxygen required for CO_2 to form was obtained from atmospheric air present as an impurity in the reactor, due to turbulences produced in the outlet hole.

The presence of air in the detector facilitated the formation of N_2O and NO as a result of the high temperature of the gas in the recombination chamber (around 400°C). Unlike CO_2 , the concentrations of N_2O and NO at the reactor outlet were not influenced by that of CCl_4 introduced into the plasma. On the other hand, an increase in flow-rate or microwave power supplied to the torch increased the concentrations of these species through an increased temperature of the gas and the turbulence introduced by atmospheric air in the reactor. Under the optimum conditions, the N_2O and NO concentrations at the reactor outlet were close to 500 and 250 ppm, respectively. Therefore, reduc-

ing the production of these compounds requires using lower microwave power and flow-rate levels.

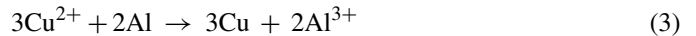
3.2.2. Solid byproducts

The reactor exhibited solid deposits in various zones after the destruction process. Such deposits were examined by X-ray diffraction spectroscopy and found to consist of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ on glass surfaces, $\text{Cu} + 5\text{AlCl}_3 \cdot 8\text{Al}(\text{OH})_3 \cdot 37.5\text{H}_2\text{O}$ on the aluminium surface of intermediate disks and CuCl on the copper of the coupler tip. A test involving the insertion of several glass, aluminium and copper sample holders in order to examine the deposition of byproducts and interactions with the reactor surfaces revealed the presence of a brown-coloured solid consisting of anhydrous CuCl_2 on glass holders removed from the plasma chamber and immediately protected from the air in order to avoid contact with atmospheric moisture (Fig. 8a) [24,25]. The corresponding X-ray pattern exhibited the typical signals for the protective plastic cover and also for a minor amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ [26] formed by partial alteration of anhydrous CuCl_2 .

If the protective plastic film was removed, moisture caused the transformation of the anhydrous copper chloride into the bluish green dihydrate, which, after 2 days, switched to a brown colour; however, the X-ray patterns exposed no change in the phases present.

The previous results were confirmed by electron microprobe analysis of the glass deposits. Once the dichloride was hydrated, a single metal (copper) was clearly observed in addition to a high content in chlorine, which confirmed the formation of a chloride.

The deposits on aluminium sample holders (Fig. 8b) obtained by protecting the samples from moisture consisted solely of anhydrous CuCl_2 . Removing the protective film, however, led to its rapid conversion into $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. The aluminium signals observed [27] corresponded to the holder. Also, the X-ray patterns revealed the presence of metal copper [28]. Taking into account that copper atoms covering aluminium atoms in the holder during the deposition of copper chloride dihydrate in vapour form, and the corresponding redox potentials, one can hypothesize the occurrence of the reaction (3):



The copper chloride dihydrate disappeared altogether after 2 days of exposure to atmospheric moisture and two phases consisting of metal copper and the decomposition product of the aluminium sample holder [viz. a hydrated hydroxychloride of formula $5\text{AlCl}_3 \cdot 8\text{Al}(\text{OH})_3 \cdot 37.5\text{H}_2\text{O}$] were observed [29].

The deposits on metal copper were slightly different from the previous ones. In fact, protecting the samples with a plastic film was indifferent as only CuCl was formed [30] and a weak signal for metal Cu due to the holder (Fig. 8c) was observed. In this

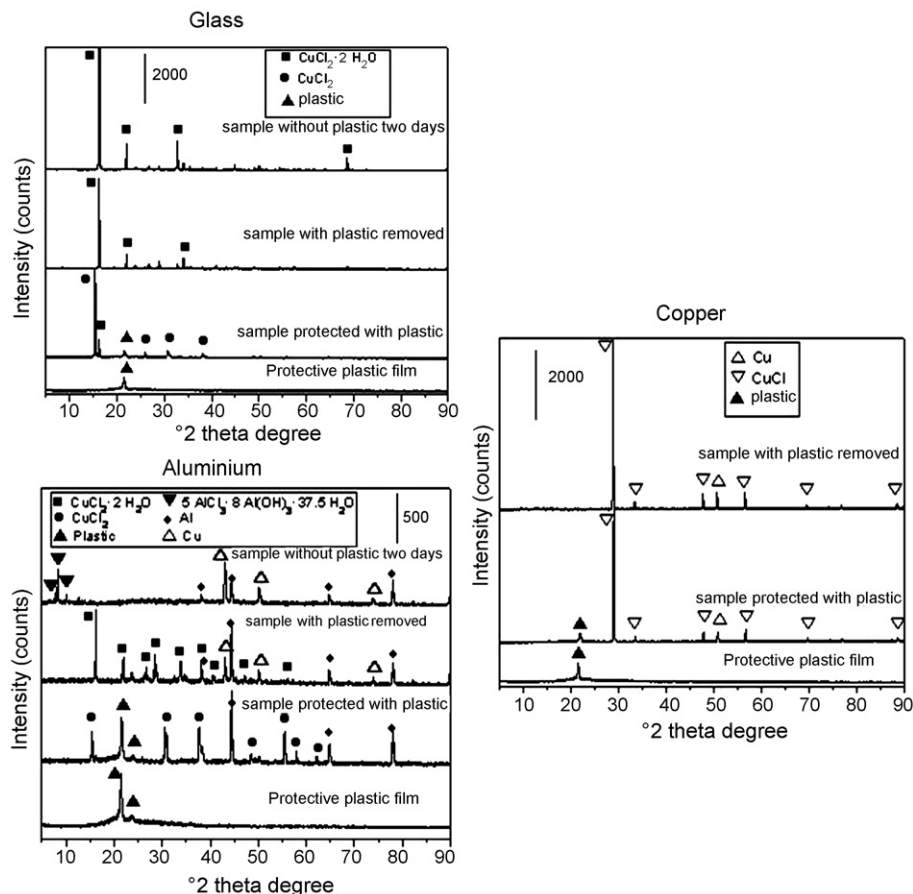


Fig. 8. XRD patterns for the solid phases deposited on glass, aluminium and copper sample holders under variable conditions in the presence and absence of a protective plastic film on the holders.

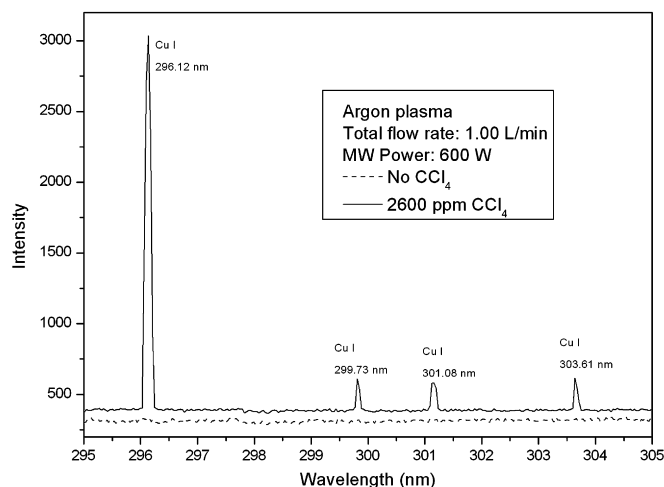


Fig. 9. Spectral lines for Cu-I in the centre of the discharge in the presence and absence of CCl_4 in the initial plasma.

case, the presence of copper facilitated the formation of CuCl instead of CuCl_2 according to the reaction (4).



3.2.3. In situ spectroscopic analysis of intermediate products

The formation of CuCl in the plasma from copper in the coupler tip was confirmed from its light emission spectrum, which contained typical lines for copper [Cu I] due to excitation of atoms detached from the coupler tip. Fig. 9 shows a region of the light emission spectrum exhibiting several lines for copper. Also, it shows the spectrum for an argon plasma containing no contaminant, which exhibited none of the copper lines observed for the same plasma but containing 2600 ppm CCl_4 . As can be seen, copper was only detached from the coupler tip when the plasma contained some contaminant, which allowed it to react with fragmented chlorine and form CuCl .

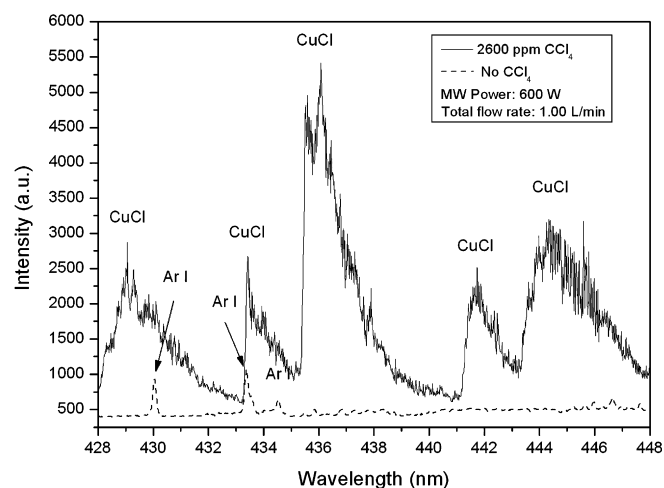


Fig. 10. Rotational bandheads for CuCl in the centre of the discharge in the presence and absence of CCl_4 in the initial plasma. Some spectral lines for Ar-I can be seen in the spectrum obtained in the absence of VOC.

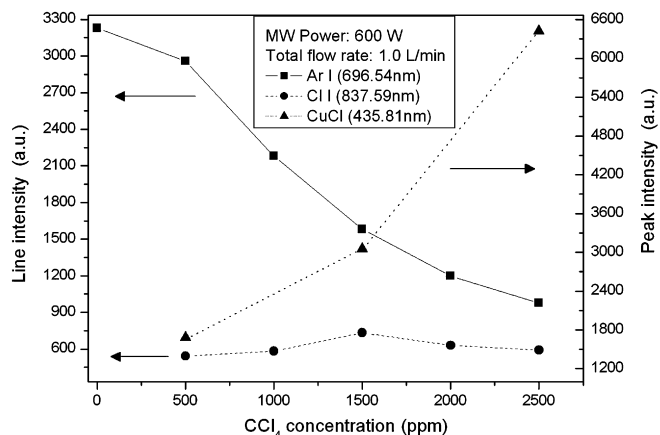


Fig. 11. Variation of the intensity of the Ar and Cl lines, and the CuCl bandhead, as a function of the initial concentration of CCl_4 in the argon plasma.

Fig. 10 shows some rotational bands for CuCl in a plasma containing 2600 ppm CCl_4 that was subjected to a microwave power of 600 W at an argon flow-rate of 1.0 L/min as compared with the spectrum for the same plasma in the absence of contaminant. The appearance of these bands as a result of introducing CCl_4 into the plasma is consistent with deposition on the reactor surfaces.

The formation of this compound is the main pathway for the loss of chlorine; as noted earlier, this avoids the release of Cl_2 and other hazardous chlorinated species. In order to confirm that increasing the concentration of CCl_4 introduced in the plasma would not raise that of chlorine released, but that of CuCl formed, we examined the intensity of the CuCl bandheads and the Ar I and Cl I lines in the presence of variable concentrations of CCl_4 in the plasma. Fig. 11 shows the results for two lines and one band. As can be seen, increasing the contaminant concentration in the plasma decreased the argon line and had virtually no effect on the chlorine line; by contrast, it increased the CuCl band in proportion.

The spectra were also found to contain bands for CN , C_2 and N_2^+ . The molecular bands and atomic lines for species in the plasma flame will be analysed in future work.

4. Conclusions

The proposed system for destroying volatile organic contaminants is an effective tool for the removal of carbon tetrachloride. By using the minimum microwave power (300 W) and a flow-rate of gas within the optimum range at each coupler tip diameter, one can reach an energy efficiency of up to 3000 g/kW h at the highest possible flow-rate and concentration levels.

The extent of CCl_4 destruction increases with increasing concentration of contaminant in the plasma.

Based on the analysis of byproducts, the CCl_4 concentration at the reactor outlet following treatment in the plasma is in the parts-per-billion region under optimum conditions and the main pathway for the loss of chlorine is the formation of a copper chloride deposit on the reactor surfaces. This is consistent with the spectroscopic measurements, based on which the intensity of the bandhead for CuCl increases while that of atomic chlorine

remains constant as the amount of CCl_4 present in the plasma increases. CuCl is less toxic and easier to handle than CCl_4 ; also, it can be used for various purposes. Therefore, the proposed method suppresses the most serious hazards of the initial compound by fixing chloride in a solid, non-volatile form.

The method must be implemented at low microwave power and flow-rate levels in order to avoid the production of N_2O and NO . Although these two species appear at substantial concentrations if the operating conditions ensuring maximal destruction are used, the proposed system allows one to use flow-rate and microwave power values over wide enough ranges to ensure minimal environmental contamination with a high energy efficiency.

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