

Production of Chloride and Hypochlorite for Analytical Purposes by Sonochemical Degradation of Organochlorines

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Neste trabalho foram enfatizadas as potencialidades da geração sonoquímica de reagentes pela irradiação ultra-sônica de resíduos de organoclorados de efluentes laboratoriais com a produção de soluções de cloreto e hipoclorito para propósitos analíticos. Foi avaliada a dependência entre a produção de cloreto obtida pela sonicação de efluentes contendo organoclorados e o tempo de irradiação para CCl_4 , CHCl_3 , CH_2Cl_2 e do inseticida Thiamethoxam[®]. Sob condições de saturação pôde ser observada a maior produção de cloreto para CHCl_3 . O processo sonoquímico de geração de cloreto mostrou boa precisão (RSD < 10%). A extensão da geração sonoquímica de hipoclorito foi também avaliada quando conduzida em presença de concentrações diferentes de NaOH. O hipoclorito gerado pela degradação de resíduos foi monitorado pelo método de Berthelot, empregado para a determinação de NH_4^+ . Os resultados da produção de azul de indofenol obtidos com soluções de hipoclorito geradas sonoquimicamente foram comparados, para diferentes concentrações de NH_4^+ , com solução comercial do reagente e nenhuma diferença significativa (nível de confiança de 95%) foi constatada.

This work was aimed at highlighting the potentialities of the reagent generation by ultrasonic irradiation to produce chloride and hypochlorite solutions for analytical purposes derived from the residues of organochlorines of laboratory effluents. The dependence between the production of chloride obtained from the sonication of effluents containing organochlorines and the irradiation time was evaluated for CCl_4 , CHCl_3 , CH_2Cl_2 and Thiamethoxam[®]. It was observed that under saturation conditions the production of chloride was highest for CHCl_3 . Additionally, good precision related to the sonochemical generation of chloride was achieved (RSD < 10%). The extent of sonochemical generation of hypochlorite was also evaluated in the presence of different NaOH concentrations. The hypochlorite generated by the degradation of CCl_4 residues was monitored by the reference Berthelot method for NH_4^+ determination. The results obtained with hypochlorite solution sonochemically generated for different NH_4^+ concentration were compared with the conventional reagent and no significant difference (95% confidence level) was found.

Keywords: ultrasonic irradiation, sonochemical degradation, reagent generation, chloromethanes, hypochlorite generation

Introduction

Most laboratories make use of processes and systems for chemical analysis, which result in the production of dangerous residues. Among the diverse possibilities for the treatment of chemical residues, the ultrasonic

irradiation has been exploited as an interesting alternative for the reutilisation of residues on a laboratory scale due to the extreme conditions currently present in the sonochemical process.¹

Sonochemical processes are related to chemical effects produced during the irradiation of low frequency ultrasonic waves (between 20 and 1000 kHz) on liquids.² The ultrasound irradiation leads to the production of acoustic

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cavitation bubbles (*i.e.* transient bubbles) in a liquid bulk during the successive rarefaction and compression phases. These bubbles expand during rarefaction phases, and molecules of gases or vapours present in the irradiated liquid medium travel to the bubbles. However, a cavitation bubble collapse when a critical diameter is attained.¹ The acoustic collapse of bubble produces $T > 5200$ K and $P > 100$ MPa, leading to homolytic cleavages of chemical bonds, giving rise to free radicals production.² The production of free radical can take place even in situations as simple as the ultrasonic irradiation of pure water.^{3,4} In this way, the sonochemical generation of reagents can deal with primary species, such as the radicals H and OH, and/or secondary species, such as H_2O_2 produced by rearrangement of OH radicals.

The generation of oxidizing species was also achieved for aqueous chloromethane solutions by irradiating with low frequency ultrasounds.⁵ In spite of the important and effective processes to decompose organochlorines,⁶⁻⁸ the sonochemical degradation has singular particularities since laboratory residues could be used for the generation of primary or secondary reagents, employing concepts of recycling or reutilisation of chemical products.⁹ The generation of free radicals and production of stable reagents in systems aided by low frequency ultrasounds occur in the sonochemical process for reutilisation of CCl_4 residue in water. The potentialities for reagent generation by low frequency ultrasonic irradiation, namely for the production of chloride and hypochlorite solutions from the reutilisation of residues of volatile chloroalkanes and a chloride herbicide present in laboratory effluents was demonstrated in this work.

Material and Methods

Reagents and solutions

The solutions were prepared with deionised water and the reagents needed for the determinations were of analytical grade. The solutions and biphasic mixtures of organochlorines were obtained by the addition of liquid residues from chromatographic analysis in water. The liquid residues were derived from a poly(ethylene) quality control laboratory which were constituted mainly by CCl_4 and low quantities of hexane, methanol, acetonitrile and poly(ethylene) fragments. The laboratorial effluent containing residues of the herbicide Thiamethoxam[®] (Novartis, 25%, m/m) was obtained from solutions of this herbicide used to develop the chromatographic determination procedure.

For chloride determinations a continuous flow system with potentiometric detection was used. The aqueous

carrier solution for flow system was prepared in order to obtain a solution $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ (Merck, Germany) and $10 \text{ } \mu\text{mol L}^{-1} \text{ NaCl}$ (Vetec, Brazil). Tests for the sonochemical production of chloride obtained from the decomposition of organochlorines were undertaken by comparison with the analytical signals provided for the chloride standard solutions in the concentration range from 0.1 to 100 mmol L^{-1} . The chloride standard solutions were prepared from the appropriate dilutions of a $1 \text{ mol L}^{-1} \text{ NaCl}$ stock solution.

The 100 mg L^{-1} stock solution of 3-(2-chloro-tiazol-5-ilmethyl)-5-methyl-[1,3,5]oxadiazinan-4-iliden-*N*-nitroamine, Thiamethoxam[®] (Novartis, USA), used in the preparation of the standards for the chromatographic procedure was prepared by weighting. The experiments with the Thiamethoxam[®] were justified since it is widely used in the husbandry of tomatoes and of other vegetables in Bahia (Brazil) in the fight against the white fly plague.

The aqueous solutions saturated with organic solvents (CH_2Cl_2 , $CHCl_3$ and CCl_4) were prepared from residues of chromatographic and infrared spectrophotometric determinations. These solutions containing the organic solvents were immediately prepared before ultrasonic irradiation by the addition of 2 mL of solvents in 100 mL of water. Soon after this, the mixtures were subjected to magnetic agitation for 2 h at 15 ± 1 °C. Following a few minutes in repose, the aqueous phase was separated and submitted to ultrasonic irradiation treatment. Additionally, for the generation of hypochlorite in highest concentration, a saturated aqueous solution with residual CCl_4 was used. However, for these assays the saturated solutions were prepared in 0.1 and $0.01 \text{ mol L}^{-1} \text{ NaOH}$ (Quimex, Brazil).

The stock solution of $100 \text{ mg L}^{-1} \text{ NH}_4\text{Cl}$ (Quimex, Brazil) was prepared by weighting and the reagent solution for ammonium determination (RS), containing 1.25 mol L^{-1} salicylate (J. T. Baker, UK), $0.9 \text{ mol L}^{-1} \text{ NaOH}$ and 0.4 mmol L^{-1} nitropruside (Vetec, Brazil) was daily prepared. The monochloramine produced from the hypochlorite generated by sonochemical effect was compared with reference solutions of monochloramine, prepared by mixing ammonium solutions of several concentrations and 0.20% (m/v) hypochlorite (A Formula, Brazil), in $0.01 \text{ mol L}^{-1} \text{ NaOH}$.

Apparatus

An ultrasonic bath (40 kHz and 90 W) Aquasonic 75D (VWR, N. York, USA) was employed for irradiation. The ultrasonic irradiation was always carried out in 10 mL borosilicate sonoreactor covered with Parafilm[®], by fixing the position of the reactor in the region of highest acoustic

incidence and maintaining the level of the solution in the sonoreactor equal to the water level in the ultrasonic bath.¹⁰ The temperature during sonication was maintained at 15 ± 1 °C with a Tecnal TE184 thermostatic bath (Piracicaba, Brazil).

The spectrophotometric determinations were made with a Femto 700 plus UV/VIS spectrophotometer (S. Paulo, Brazil). Chloride determinations were undertaken with a Micronal B374 millivoltmeter (S. Paulo, Brazil) equipped with an ion selective electrode with crystalline membrane for chloride and AgCl/Ag as reference electrode (model 900029/5, Thermo Russel, UK). The tubular ion selective electrode with a crystalline membrane for chloride was constructed according to a procedure earlier described.¹¹ The pH measurements were made using a DM-21 pH meter (Digimed, S. Paulo, Brazil) with a glass electrode (model 01D2590, Digimed, Brazil).

Low dispersion flow manifold for the potentiometric determination of chloride generated by sonochemical action (Figure 1) was made up with a three-way solenoid valve (NResearch 161T031 - Stow, MA, USA) for sampling the sonication product at defined time intervals, a peristaltic pump Gilson Minipuls 3 (Villiers le Bel, France) for aspiration of the sample (S) and carrier solution (C), control interface and data acquisition (PCL 711S - Advantech, Taipei, Taiwan), together with a Pentium I microcomputer (PC). The system was controlled by software developed in QuickBASIC 4.5 language.

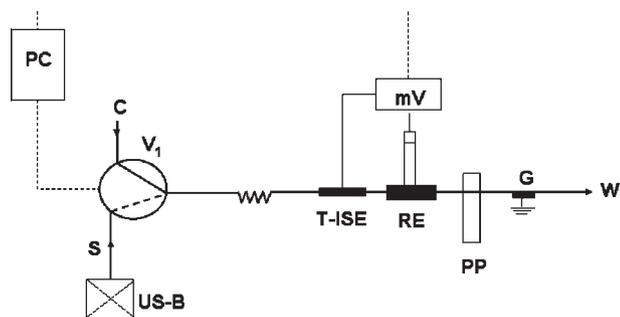


Figure 1. Low dispersion flow manifold to monitor chloride production from sonochemical degradation of chlorinated organic compounds. V1: solenoid valve; C: carrier solution; S: sample; US-B: sonication device; T-ISE: tubular ion selective electrode; RE: reference electrode; mV: millivoltmeter; PP: peristaltic pump; G: ground electrode; W: waste; PC: microcomputer

Procedures

All liquid residues were previously filtered in a fritted funnel to separated poly(ethylene) fragments. The liquid residues were previously classified according to their chemical constitution, in order to select liquids with high concentration of respective chloromethane (CCl_4 , CHCl_3 and CH_2Cl_2) for the following assays. The optimal

conditions for reagent production were studied concerning to the temperature, the sonication time and chemical environment.

The generation of chloride from sonication of aqueous solutions saturated with organic solvent was undertaken at a temperature of 15 ± 1 °C (to restrain evaporation losses) by using the flow system (Figure 1). For these assays, 5 mL of the aqueous solutions saturated with organic residues were subjected to irradiation (US-B). The chloride resulting from the sonication was monitored (mV) with a tubular ion selective electrode for chloride (T-ISE). At each 10 s of sonication, 77 μL of sonicated solution were aspirated by PP in the analytical path by activating the three way solenoid valve (V_1) during 2s. Between consecutives sample insertions, V_1 was switched to the carrier solution (C) and the S zone in the analytical path was directed to the detector at a flow rate of 2.3 mL min^{-1} . The valve activation and data acquisition were controlled by PC, as earlier described.¹²

The assays with the residual solution of the Thiamethoxam® were carried out by sonicating 5 mL of 100 mg L^{-1} of the herbicide solution in interval range from 10 to 60 min. After sonication, the chloride generated by sonochemical effect and the pH were measured.

The experiments involving the hypochlorite production were always carried out using residues containing mainly CCl_4 . Since CCl_4 has extremely low miscibility in water, its maximum concentration in the aqueous solution at a fixed temperature is easily attained. Hypochlorite generation was evaluated by varying the NaOH concentration and the irradiation time and maintaining the parameters related to ultrasonic irradiation conditions as previously referred. The sonication was carried out alkalizing the aqueous phase, so that the aqueous solutions had final NaOH concentration equal to 0.1 or 0.01 mol L^{-1} . The hypochlorite production by sonochemical degradation of CCl_4 for sonication time up to 5 min was indirectly monitored by Berthelot method,¹³ adding 0.1 mL of 1 mg L^{-1} NH_4^+ solution to the sonicated solution. After the monochloramine production, 2 mL of RS were added and diluted to 10 mL prior the measurement at 645 nm. In order to evaluate the analytical usefulness of the hypochlorite generated a set of experiments were carried out with reference NH_4^+ solutions in the concentration range from 0.25 to 2 mg L^{-1} .

Finally, studies were performed to evaluate the extent of hypochlorite generation by the ultrasonic irradiation in biphasic systems. In order to attain this goal, 100 mL of a 0.01 mol L^{-1} NaOH solution containing 500 μL of laboratory effluent sample containing predominantly CCl_4 and different amounts of hexane, acetonitrile and methanol

were subjected to ultrasonic irradiation over 120 min for the production of aqueous hypochlorite solution. After the sonication, 400 μL of the resulting aqueous solution were submitted to the Berthelot method, as previously described, employing NH_4^+ reference solutions from 0.5 to 5 mg L^{-1} . To validate the proposed method for hypochlorite generation, the same procedure was carried out with a prepared 0.20% (m/v) ClO^- solution.

Results and Discussion

The capacity to break chemical bonds by acoustic cavitation, characteristic of the action of high power ultrasounds in liquid media, makes any substance that contains atoms of a common element with the reagent to be produced, could be considered as a possible precursor. Therefore, the sonication of an aqueous solution of chloroalkanes is a potential source of Cl^- , Cl_2 and HClO .^{14,15} The tendency for one or other species to prevail depends on the physical and chemical properties of the precursor, specially the hydrophobicity, vapour pressure, molar mass and concentration.^{2,16}

Production of chloride from chloroalkanes

The degradation of chloromethanes in aqueous solutions by employing ultrasonic bath aimed at a time based control of chloride generation, since with this ultrasonic generator the conversion rate is small, allowing to produce only the strictly necessary species amount. Therefore it can be considered as a viable and versatile alternative to reuse these residues for analytical applications.

In order to evaluate the amount of chloride generated and the repeatability of sonication process, three independent solutions saturated with CHCl_3 and CCl_4 were submitted to the ultrasonic irradiation in the same conditions for several irradiation time (Table 1). For this purpose the analytical signals were obtained by direct potentiometry and the results have pointed out to an adequate rate of chloride production with precision higher than 90%. The same procedure was carried out for ten independent samples of both chloromethanes in order to evaluate the repeatability of the proposed process for chloride generation from solutions saturated with CHCl_3 and CCl_4 after 3 min of irradiation and 10% and 9% for RSD was respectively obtained. Therefore possible losses associated with device employed for sonication did not affect the usefulness of the ultrasonic reagent generation for analytical propose.

The chloride profiles dependence on sonication time

Table 1. Potentiometric data (mV) and generated chloride concentration (mmol L^{-1}) for 1, 3 and 5 min of sonication from saturated aqueous solutions of CCl_4 and CHCl_3

t_{us} (min)	CCl_4^*		CHCl_3^*	
	mV	mmol L^{-1}	mV	mmol L^{-1}
1	-33.7 ± 0.6	0.205 ± 0.005	-45 ± 1	0.33 ± 0.01
3	-53 ± 2	0.46 ± 0.04	-63 ± 1	0.72 ± 0.04
5	-63 ± 1	0.72 ± 0.03	-78 ± 1	1.37 ± 0.08

*mean values and standard deviations from 3 independent sonicated solutions.

for the evaluated chloroalkanes (CH_2Cl_2 , CHCl_3 and CCl_4) are depicted in Figure 2. It was initially observed that the chloride concentration had increased by increasing the sonication time and a plateau would be attained for a long time of irradiation. Therefore in order to obtain high chloride concentration the sonication time must be longer.

The extent on Cl^- production (Figure 2) was quite high after the initial seconds of ultrasonic irradiation. It can be explained since all evaluated chloroalkanes had low molar masses and hydrophobicity and high vapour pressures. However, it can be observed in Figure 2 that the extent on chloride production was also dependent on the number of chlorine atoms present in the precursor and on the solubility in aqueous medium, which pointed out the tendency of a molecule of precursor to migrate to the gas phase of the cavitation bubble. The highest chloride production was observed for CHCl_3 (Figure 2). This result could be related to its high concentration in aqueous solution in saturation conditions, since the solubility of CHCl_3 in water is about 10 times higher than CCl_4 (0.82 and 0.08 g in 100 g of water, at 20 $^\circ\text{C}$, respectively). Notwithstanding, for the same concentration of chloromethanes in aqueous solutions, it would be expected

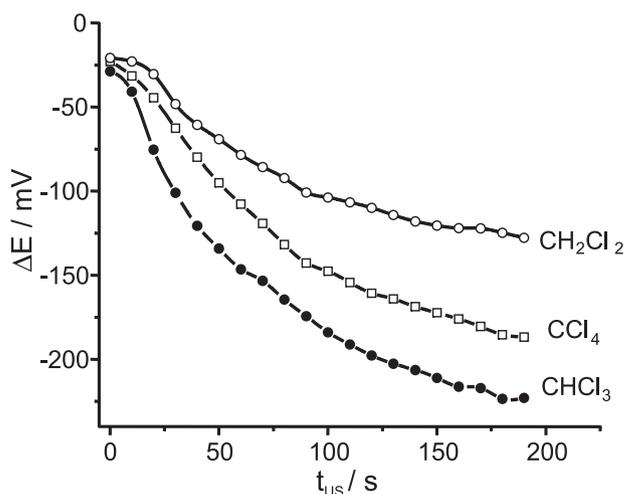


Figure 2. Variation of the potential difference between chloride ion selective electrode and reference electrode (mV) in aqueous solutions saturated with CH_2Cl_2 , CHCl_3 and CCl_4 during sonication (t_{us}).

higher chloride production for CCl_4 , in view of its higher hydrophobicity, number of chlorine atoms and vapour pressure.

In spite of the higher solubility of CH_2Cl_2 (2 g in 100 g of water at 20 °C) when compared with CHCl_3 and CCl_4 , the production of chloride from the sonication of solutions saturated with CH_2Cl_2 was the lower (Figure 2). This fact can be explained by the number of chlorine atoms in the molecule, its low hydrophobicity and low vapour pressure. Additionally, under saturated conditions, the high CH_2Cl_2 concentration endangers the cavitation phenomena, due to no-transient bubbles could be produced in the presence of large quantity of volatile species. This fact was confirmed by the sonication of more diluted CH_2Cl_2 solutions by increasing irradiation times, leading to a higher chloride concentrations.

Production of chloride from Thiamethoxam® aqueous solution

Assays with residues of 3-(2-chloro-tiazol-5-ilmethyl)-5-methyl-[1,3,5]-oxadiazinan-4-iliden-*N*-nitroamine, Thiamethoxam®, were also carried out to obtain information from sonochemical degradation of a high molar mass organochlorine compound (291.71 g mol⁻¹). The generation profile of chloride and the pH variation of the solution containing the herbicide with the irradiation time can be observed in Figure 3. As mentioned elsewhere, for this organic compound, the chloride production was diminished, due to its high molar mass, low vapour pressure and low hydrophobicity. Notwithstanding, the high solubility of Thiamethoxam® residues in water, its molecules did not tend to migrate to the cavities, since the vapour pressure and hydrophobicity were prevalent parameters and any degree of degradation for this compound necessary occurred in the bulk solution.

The generation of chloride by sonochemical degradation was associated with a pH decrease. The similarities between the profiles of chloride generation, expressed in mV, and pH variation illustrated in Figure 3 should be highlighted. It is probable that the degradation of organic chloride compounds of high molar mass is initiated when the molecules of organic compound are attacked by the hydroxyl radicals derived from the cavitation. This liberates chlorine radicals that for their parts interact with water molecules to generate HCl and further OH radicals, feeding the chain of reactions. By this reaction model the concentrations of Cl^- and H^+ in irradiated medium should be increased in the same proportion with the sonication time. As the pH and the potential difference between the ion selective electrode

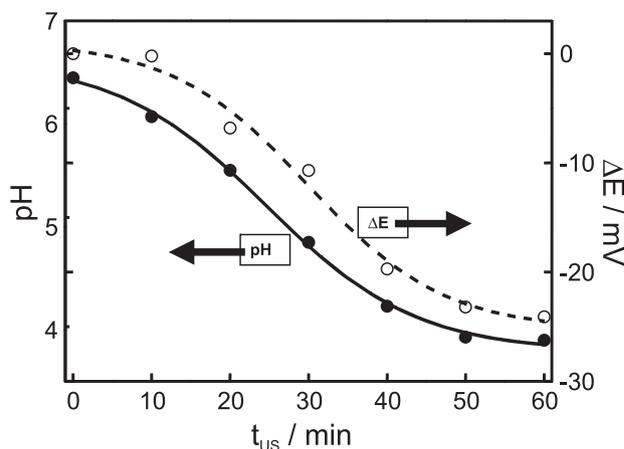


Figure 3. Effect of the sonication time (t_{US}) on the chloride production (ΔE) and pH variation on 100 mg L⁻¹ Thiamethoxam® solution.

and the reference electrode, expressed in mV, are related to the logarithm of H^+ and Cl^- concentration, respectively, the same profiles of the curves depicted in the Figure 3 suggest that reaction model described above for the HCl production by the herbicide sonolysis is possible and it occurs in the bulk of irradiated solution.

Sonochemical hypochlorite generation for the determination of NH_4^+

Aqueous solutions containing residues of CCl_4 when irradiated with low frequency ultrasonic waves lead to the Cl_2 production as well. Nevertheless by alkalinizing the medium with NaOH before ultrasonic irradiation, a hypochlorite solution will be produced. Since the irradiation conditions for ultrasonic bath was optimized as previously described and the temperature was fixed, the extent of hypochlorite production was only dependent on the sonication time and the alkalinity of irradiated medium. The Berthelot method was employed to monitor the hypochlorite production by measuring the signals related to indophenol produced for 1 mg L⁻¹ NH_4^+ solution (Figure 4). As mentioned elsewhere, the effect of the alkalinity was investigated for 0.1 and 0.01 mol L⁻¹ NaOH solutions saturated with CCl_4 . It was observed that, irrespective of the concentration of NaOH, the increase in sonication time resulted in an increase in hypochlorite production. Additionally, a higher production of monochloramine was observed for hypochlorite solutions prepared by sonication of the solution containing CCl_4 in 0.01 mol L⁻¹ NaOH solution (Figure 4). It can be explained since the monochloramine is preferentially generated in the pH range between 8 and 11.¹⁷

The use of the reagents generation for analytical purposes was explored for NH_4^+ determination, changing the sonication time of the aqueous solution containing

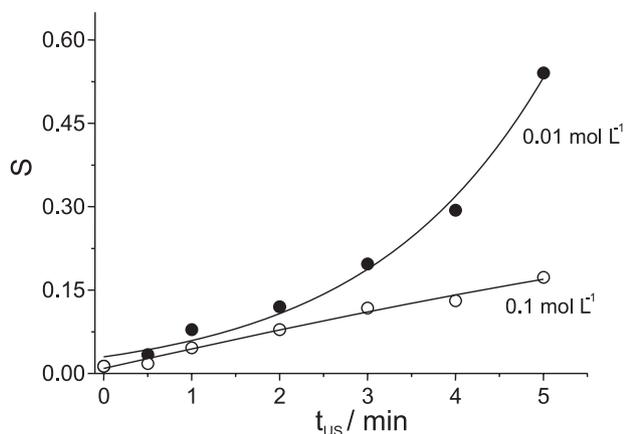


Figure 4. Variation of the analytical signal (S) with the sonochemical hypochlorite production for 0.1 and 0.01 mol L⁻¹ NaOH solutions saturated with CCl₄ up to 5 min of sonication.

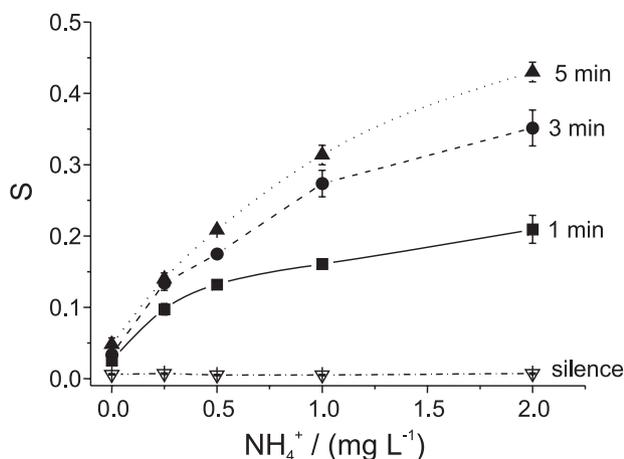


Figure 5. Evaluation of the sonication time (t_{US}) effect for hypochlorite generation in 0.01 mol L⁻¹ NaOH solution saturated with CCl₄, monitored by the analytical signal related to indophenol blue production (S) for ammonium concentration up to 2 mg L⁻¹.

the hypochlorite precursor agent (CCl₄). As can be observed in Figure 5, for all assays carried out with sonication there was a generation of indophenol blue, which can be related to the production of hypochlorite, and consequently of monochloramine. However, for the tests carried out under silence condition ($t_{US} = 0$), no variation in analytical signal with the increase in ammonium concentration was observed. Also in this investigation (Figure 5), the dependence on the analytical signal obtained with sonication time could again be observed, through the higher return in the formation of indophenol blue by increasing irradiation time. Apart of this, for different irradiation periods ($t_{US} > 0$), the increase in NH₄⁺ concentration led to an increase in the analytical signal (S) measured at 645 nm and, then in the indophenol concentration. However, due to the generated quantity of hypochlorite being insufficient to react with the NH₄⁺ ions added to the irradiated medium, the tendency for the analytical signal to stabilise with the increase in NH₄⁺

concentration could be evidenced for the different irradiation time.

Under CCl₄ saturation condition, the ammonium conversion to monochloramine must be quantitative for samples of low NH₄⁺ concentrations. Therefore, as can be observed in Figure 5, for samples of low NH₄⁺ concentration (< 1.0 mg L⁻¹), the sonication time must be sufficiently long (≥ 3 min) to allow the quantitative conversion to monochloramine of the NH₄⁺ present in the sample. On the other hand, for high quantity of ammonium (> 1.0 mg L⁻¹), the analytical feasibility is reached, only if a low quantity of the analyte (NH₄⁺) is converted to monochloramine and, to this end, the sonication time interval must also be small ($t_{US} \leq 1$ min). In this way, the quantity of monochloramine produced by reaction between the ammonium ions with the small quantity of the generated hypochlorite will be directly proportional to the analytical signal (Figure 5) related to 1 min of sonication.

Usually, for spectrophotometric methods, the addition of a reagent excess is preferred in order to increase the extent of the reactions. However, it is interesting to note that in order to increase the quantity of hypochlorite sonochemically generated, the quantity of CCl₄ must be increased as well. In this way, the irradiation would not be carried out in a homogenous system, but with the addition of a higher quantity of liquid residue containing CCl₄ to form a biphasic system with water. However, to ensure that this greater quantity of the precursor can be degraded and converted to hypochlorite, the sonication time must be increased to tens of minutes.

The concentrations of NH₂Cl obtained from the solution prepared after sonication of the heterogeneous system (0.01 mol L⁻¹ NaOH solution and residue of CCl₄) as well as from the solution of commercial hypochlorite after the addition of NH₄⁺ solutions with concentrations up to 5 mg L⁻¹ are summarised in Table 2. It could be verified that the quantity

Table 2. Evaluation of chloramine concentration produced for different NH₄⁺ concentration by 0.1% (m/v) hypochlorite and the hypochlorite solution generated after 120 min of sonication of 100 mL of 0.01 mol L⁻¹ NaOH solution and 500 μ L of CCl₄ residues

NH ₄ ⁺ (mg L ⁻¹)	Chloramine produced / (mg L ⁻¹)	
	0.1% (m/v) HClO added	produced by sonolysis
0	0.05	0.06
0.5	1.25	1.50
1	2.74	2.99
2	5.93	5.86
3	8.84	8.74
4	11.3	11.6
5	14.2	14.2

of hypochlorite generated by ultrasonic irradiation of the biphasic mixture containing the precursor (CCl_4) was sufficient to produce monochloramine quantities comparable to those produced by employing a 0.20% (m/v) hypochlorite solution (Table 2). By applying *t-test* paired for 95% confidence level no significant difference was verified for both hypochlorite solutions. Residues from chemical analysis laboratories, containing elevated quantity of CCl_4 or other organic chloride solvents can be used as reagent precursors, namely for NH_4^+ determination in different matrices.

Conclusions

The examples here presented are applications of the ultrasonic waves for the degradation and generation of reagents, starting from a single class of precursor substances (organochlorines). The degradation of harmful substances associated with the use of their products, as well as the production of the quantity of reagent strictly necessary for carrying out the reactions involved in an analysis were demonstrated. From the perspective of cleaned analytical procedures, the decontamination of laboratory effluents, aided by ultrasounds in the same laboratory, opens up a vast field of research by increasing the search for (i) precursors, (ii) reaction routes and (iii) feedback solutions.

Acknowledgments

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