

Mercury determination by FI-CV-AAS after the degradation of organomercurials with the aid of an ultrasonic field: The important role of the hypochlorite ion

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Received 14 January 2005; received in revised form 28 April 2005; accepted 8 June 2005

Available online 22 July 2005

Abstract

Due to new findings, the methodology based on room-temperature ultrasonic irradiation (sonolysis) for conversion of organomercurials into inorganic mercury [J.L. Capelo, I. Lavilla, C. Bendicho, *Anal. Chem.* 72 (2000) 4979–4984.] is further investigated. Inorganic mercury is selectively determined by Flow Injection-Cold Vapour Atomic Absorption Spectrometry (FI-CV-AAS) using SnCl₂/HCl. Complete oxidation of methyl-mercury can be accomplished within 90 s whilst phenyl and diphenyl-mercury can be degraded within 10 s using a 50% sonication amplitude (100 W nominal power) provided by a probe ultrasonic device (20.5 kHz frequency) and a 1 mol L⁻¹ HCl liquid medium with the presence of hypochlorite ion. The importance of hypochlorite in reduction of organomercurials by stannous chloride is highlighted. Oxidation kinetics indicated a pseudo first-order reaction for methyl-mercury, phenyl-mercury, and diphenyl-mercury.

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Keywords: Organomercurials; Focused Ultrasound; Degradation; Hg; FI-CV-AAS

1. Introduction

Mercury is a well-known toxic metal with a devastating effect over the living organisms due to its affinity by the sulphur groups present in many enzymes and proteins. The mercury can be bio-accumulated in the body and in the long-term causes organ dysfunction and severely affects the central nervous system of the human body.

Mercury can be found as the inorganic form Hg²⁺ and, as a result of the bacterial methylation, it can be also found as organomercury in the form of methyl-mercury [2].

Total mercury determination in water and wastewater has been done mainly by Flow-Injection Cold-Vapour Atomic Absorption Spectrometry (FI-CV-AAS), and requires that mercury be released from organomercurials present in the sample prior to its determination. To achieve this objective different attempts have been published, based on off-line or on-line degradation of organomercury compounds, with a variety of reagent combinations [3–6]. The degradation in water and wastewater of organomercurials under an ultrasonic field provided by a probe sonicator was first described by Capelo et al. [1]. Advantages of this procedure are (i) simplicity, (ii) removal of hazardous wastes, (iii) losses of mercury by volatilization are diminished, and (iv) rapid sample treatment. Despite the environmental and experimental advantages of the aforementioned procedure, little has been

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done since its publication in order to improve the methodology or to study its application in analytical procedures. In this work, we present critical new findings regarding the degradation of organomercurials. The importance of hypochlorite ion in the presence of hydrochloric acid during degradation is highlighted. Further advantages of the proposed method over existing methods which are currently employed for oxidation prior to total Hg determination are the removal of hazardous wastes, the decreased risk of Hg losses by volatilization, and the high throughput due to the short time needed for the oxidation procedure.

2. Experimental section

2.1. Apparatus

The flow injection system used for cold vapour generation consisted of a four channel Gilson (Villiers le Bel, France) Minipuls 2 peristaltic pump, a Perkin-Elmer (Überlingen, Germany) membrane gas–liquid separator, a four-way Rheodyne (Supelco, Bellefonte, PA) injection valve with a 500- μ L loop, and a Fisher and Porter (Warminster, PA) flow meter (0–100% N_2). Tygon tubing of different internal diameters was used for carrying the reducing agent, carrier solution, carrier gas and waste solution. The initial conditions for cold vapour generation using $SnCl_2/HCl$ as a reducing agent were established in a previous work [1] in which a similar FI system was used and were: 1% mass/v $SnCl_2$ solution stabilized in 1% (v/v) HCl; 3 mL min^{-1} ; 3% (v/v) HCl solution used as carrier, 10 mL min^{-1} . A 200 mL min^{-1} flow-rate of carrier gas (N_2) was used. A Branson Sonifier 150 ultrasonic cell disruptor-homogenizer (100 W, 22.5 kHz, Branson Ultrasonics Corporation, USA) equipped with a 6-mm titanium micro-tip was used. Ultrasonic energy irradiation was fixed using a power setting in the 50% range. The Sonifier 150 has a digital LCD display, which provides a continuous read-out of the watts delivered to the end of the probe (range 8–10 W in this work, warning: ultrasonication must be performed with care; manufactured safety conditions must be followed; experiments must be carried out in a fume cupboard; and hearing protection must be used). Mercury atomic absorbance was measured with a Varian (Cambridge, UK) atomic absorption spectrometer model SpectrAA 20 plus equipped with a homemade quartz tube. The quartz tube was kept at room temperature during operation. A mercury hollow-cathode lamp operated at 4 mA was used as a radiation source. The mercury line at 253.7 nm and a slit width of 0.5 nm were used for measurements. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Model Ultima, Jobin–Yvon, France) was used to determine Al, Ca, Fe, Cu, Cd, K, Na, Si, and Zn in solutions of hydrochloric acid. The measurements of the elements were made with the following instrument parameters: plasma power 1200 kW, plasma gas flow 12 L min^{-1} . The wavelengths used are shown in Table 1.

Table 1

Figures of merit for determination of Elements by ICP-AES

Element	Wavelength (nm)	<i>r</i>	LOD (mg L ⁻¹)	Calibration range (mg L ⁻¹)
Fe	259.940	0.99989	0.0010	0.0033–1
Ca	317.933	0.99973	0.023	0.076–1
Si	251.611	0.99999	0.0019	0.063–1
Zn	213.856	0.99946	0.0009	0.003–1
Al	237.312	0.99803	0.030	0.1–1
Na	589.592	0.99954	0.0040	0.013–1
K	766.490	0.9991	0.16	0.53–1
Cd	226.502	0.9995	0.0024	0.008–1
Cu	223.008	0.9995	0.0084	0.028–1

2.2. Reagents

All chemicals were of analytical-reagent grade. Tin (II) chloride dihydrate (Merck, Darmstadt, Germany) was prepared fresh daily by dissolving the solid in HCl (Merck). An inorganic mercury stock standard solution (Merck, 1 g L⁻¹) was used. A methyl-mercury stock standard solution (100 mg L⁻¹) was prepared from methyl-mercury chloride (Riedel-de-Häen, Seelze, Germany) by dissolving the appropriate amount of the solid in pure ethanol (Merck, N 23653583704) and making up to volume with ultrapure water. Stock standard solutions (100 mg L⁻¹) of phenyl-mercury and diphenyl-mercury were prepared from the corresponding chloride salts (Riedel-de Häen, seelze, Germany). Phenyl-mercury was dissolved in pure methanol and making up to volume with ultrapure water. Magnetic agitation for 4 h was necessary. Diphenyl-mercury was dissolved in pure methanol (Merck). Sodium hypochlorite solution was purchased from Aldrich (Wisconsin, USA). All stock standard solutions were stored in a refrigerator at 4 °C and protected from light. Working standard solutions were prepared just before use by appropriate dilution of the stock standard solution. The standard stock solutions of Fe, Al, Zn, Si, Ca, K and Na (1000 mg L⁻¹) for the ICP-AES measurements were supplied by Merck. Hydrochloric acid (HA) from five different sources was used in this study. The five sources were as follows: HA I: Merck 37%, N 317.1000, packed in brown glass bottle; HA II: Riedel-de-Haën 37% N 30721 packed in translucent plastic bottle; HA III: Panreac (Barcelona, Spain) 37% N 131020.1212 packed in black plastic bottle; HA IV: Merck 37% N 317.2501 packed in translucent plastic bottle; HA V: Merck 25% N 316.1000 packed in brown glass bottle.

2.3. Oxidation procedure

Experimental solutions were prepared by mixing appropriate amounts of ultrapure water, HCl, hypochlorite solution, and nitric acid and applying sonication for various times from approximately 0 to 180 s. Sonicated solutions were analyzed within approximately 10 s after cessation of sonication. Sonication was not applied to control solutions. The concentration

of mercury (as organomercury) chosen was 30 ppb. The measurements were performed just after the sample treatment was complete. These precautions were taken because information dealing with degradation of organomercurials in literature is inconclusive. For instance, the photolytic degradation of methyl-mercury was cited [7], whereas, other authors stressed the high stability of this organomercurial under drastic conditions [8]. Although chlorine can absorb in the UV region (e.g. 253.7 nm), in our experimental conditions such interference was not observed.

3. Results and discussion

3.1. Methyl-mercury

The oxidation of methyl-mercury by sonication of solutions containing HCl from various sources is shown in Fig. 1. For HA I, IV, and V, the amount of methyl-mercury oxidized was negligible (is not significantly different from controls) when sonication time is zero (0) second and increases as sonication time increases. In the presence of hydrochloric

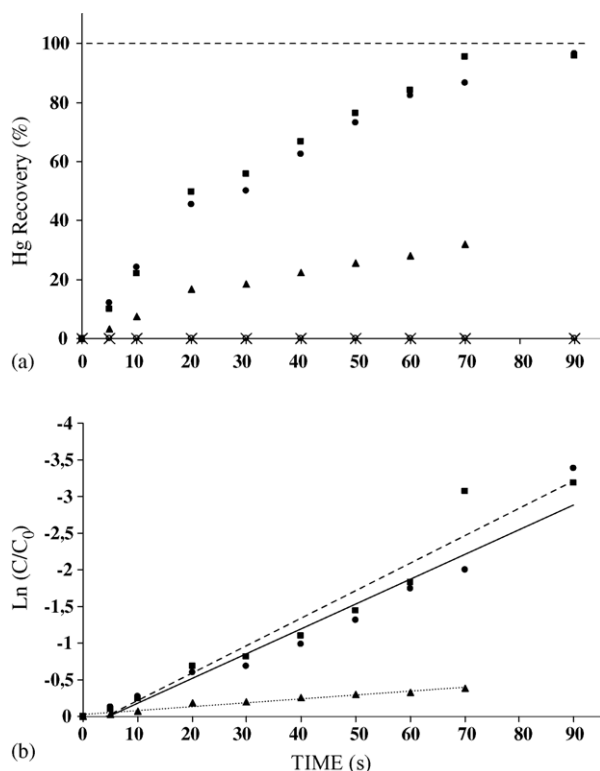


Fig. 1. (a) Oxidation of 30 ng L⁻¹ of methyl-mercury with (●) hydrochloric acid I, (○) hydrochloric acid II, (×) hydrochloric acid III, (▲) hydrochloric acid IV, (■) hydrochloric acid V. Recovery was expressed as ([Peak absorbance of MeHg⁺]/[Peak absorbance of Hg²⁺]) × 100. Ultrasonic conditions: see sample treatment. (b) First-order plot for degradation corresponding to the kinetics curves shown in (a). SnCl₂ was used as a reducing agent. *C* is the organomercurial concentration remaining at a time *t* and *C*₀ is the initial organomercurial concentration (*t* = 0).

acid I, HA I, but without sonication the solution containing methyl-mercury did not give any appreciable signal. As can be seen in Fig. 1, when focused ultrasound was applied into the sample, the methyl-mercury degradation followed an oxidation kinetic of pseudo-first-order reaction. In Fig. 1, *C* is the organomercurial concentration remaining at a time *t* and *C*₀ is the initial organomercurial concentration (*t* = 0). The reaction rate constant, *k* (s⁻¹), as calculated from experimental data was 0.0339 s⁻¹ in good agreement with data reported in a previous work [1]. When the set of experiments described above were performed with HA V, the degradation of the organic compound followed a similar kinetic process. In this case the reaction rate found was 0.0373 s⁻¹, similar to the one obtained with HA I. On the other hand, when the degradation studies were developed with the acids II and III the degradation rates for methyl-mercury were unexpectedly low. Thus, when the former acids were used, no appreciable signal from mercury was obtained after a sonication time of 60 s, and with a longer time, 180 s, the recovery of mercury was 15%, corresponding to c.a. 5 ppb. Finally, the reaction rate with acid IV was slow, but efficient since after 180 s of treatment a concentration of 20 ppb was calculated, what means that c.a. 67% of the methyl-mercury was degraded after such sonication time. No degradation occurred at 180 s in the absence of sonication in the control samples.

These results allowed us to test the different acids in conjunction with ultrasonication with other organo-mercurials.

3.2. Phenyl-mercury

The oxidation of phenylmercury by sonication of solutions containing HCl from various sources is shown in Fig. 2. Experiments with HA I were repeated three times because results were unexpected. For HA I, recovery without sonication was 55% at 20 s and 75% at 60 s. With HA I total recovery was achieved by applying ultrasounds for 10 s. These findings were unexpected and did not validate results previously reported [1]. In order to verify the aforementioned experimental data, the procedure was repeated, but this time a different acid, HA II, was used. The experiment was performed using the organomercury solution previously employed with HA I. Once again, the results were surprising: HA II did not degrade the phenyl-mercury, neither by contact nor by sonication. A third hydrochloric acid was investigated (HA III) with identical results: no degradation was observed, even with a sonication time as long as 60 s. Finally, two more acids were tested. As can be seen in Fig. 2, the oxidation rate for phenyl-mercury is faster with HA V than with HA IV. Results with HA V agree well with data reported elsewhere [1]. It should be stressed here that neither HA IV nor HA V could degrade the organomercurial without the aid of ultrasounds. As in the case of methyl-mercury, the oxidation kinetics is in good agreement with a pseudo-first-order reaction, being the reaction rate constants 0.0231 and 0.0074 s⁻¹ for HA IV and V, respectively.

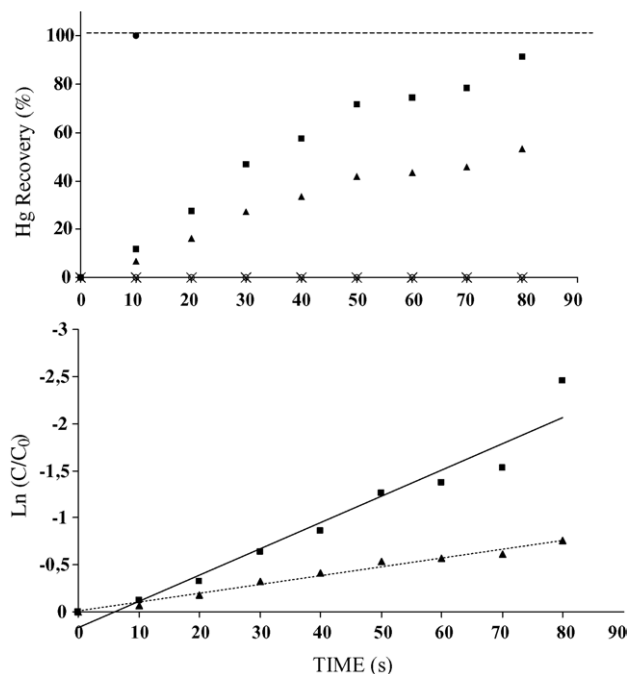


Fig. 2. (a) Oxidation of 30 ng L^{-1} of phenylmercury with (●) hydrochloric acid I, (○) hydrochloric acid II, (×) hydrochloric acid III, (▲) hydrochloric acid IV, (■) hydrochloric acid V. Recovery was expressed as $([\text{Peak absorbance of PheHg}^+]/[\text{Peak absorbance of Hg}^{2+}]) \times 100$. Ultrasonic conditions: see sample treatment. (b) First-order plot for degradation corresponding to the kinetics curves shown in (a). SnCl_2 was used as a reducing agent. C is the organomercurial concentration remaining at a time t and C_0 is the initial organomercurial concentration ($t=0$).

3.3. Diphenyl-mercury

The oxidation of diphenylmercury by sonication of solutions containing HCl from various sources is shown in Fig. 3. In the presence of HA I, the organic was degraded by contact (without ultrasounds, see Fig. 3), and after 360 s the recovery was $74 \pm 4\%$ ($n=3$). However, the reaction was dramatically improved in kinetic terms when the ultrasonic probe was used, and 100% of mercury was recovered in 10 s. With HA II–V no degradation occurred at 180 s in the absence of sonication (in controls). Negligible results were obtained with HA II and III in conjunction with sonication, but with HA IV and V plus sonication the mercury recovered after 60 s of sonication was 46 and 66%, respectively.

3.4. Role of hypochlorite ion

The results clearly showed that (a) fast degradation of organomercury compounds was only possible with acids I, IV, and V in the presence of sonication, and (b) the rate of degradation varied as follows: $\text{HA I} \gg \text{HA V} > \text{HA IV}$. The differences among these acids were the material of the container in which they were packed. Thus, HA I and V were packed in a brown glass bottle whilst HA IV was in

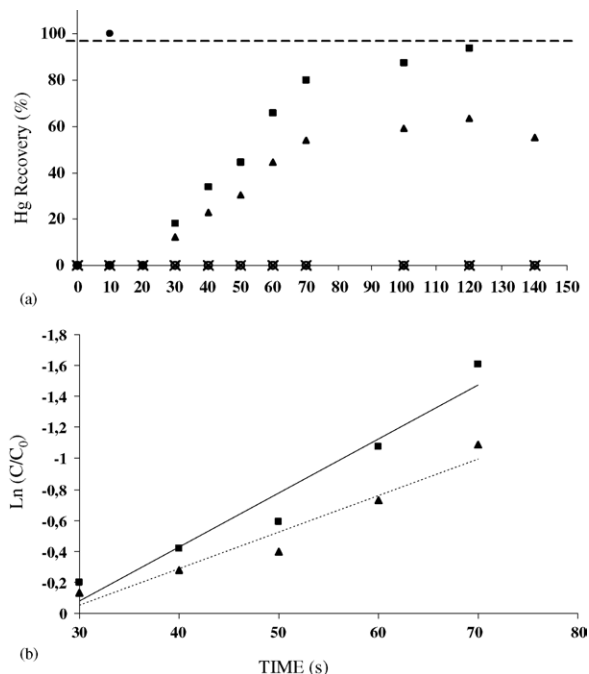


Fig. 3. (a) Oxidation of 30 ng L^{-1} of di-phenylmercury with (●) hydrochloric acid I, (○) hydrochloric acid II, (×) hydrochloric acid III, (▲) hydrochloric acid IV, (■) hydrochloric acid V. Recovery was expressed as $([\text{Peak absorbance of di-PheHg}^+]/[\text{Peak absorbance of Hg}^{2+}]) \times 100$. Ultrasonic conditions: see sample treatment. (b) First-order plot for degradation corresponding to the kinetics curves shown in (a). SnCl_2 was used as a reducing agent. C is the organomercurial concentration remaining at a time t and C_0 is the initial organomercurial concentration ($t=0$).

a translucent plastic bottle. It should be stressed here that HA I, IV and V were purchased from the same company (Merk) [disclaimer: specific company and product names are given to provide exact description of experimental details. Their mention does not imply recommendation or endorsement by the authors]. Further experiments were done to elucidate the reasons why the degradation of the organomercurials was achieved only with some specific products. Bearing in mind that the hydrochloric acid stored in the brown glass bottles was the most effective, two hypotheses were considered. The first one was to take into account that, as consequence of the contact time between the glass and the acid, the presence of some metals can act as catalysers of the degradation. It is well known that for a glass acid container the total content for some metals such as Fe or Zn can increase with time. We compared k values and element concentrations to determine whether degradation was faster with acids stored in brown glass bottles that released metals into the HCl. Nevertheless, this approach can not explain why the acid IV, which is bottled in a plastic container, can also destroy the organomercurials with the aid of an ultrasonic field whilst the procedure was not possible with other acids packed in similar containers (acids II and III). A second hypothesis dealing with the presence of hypochlorous acid was also considered as follows: hydrogen chloride is prepared industrially by the combustion of

Table 2

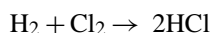
Container material concentrations ($\mu\text{g kg}^{-1}$) of elements in, and kinetic constants (s^{-1}) obtained for degradation of methyl, phenyl and di-phenyl-mercury in 1 mol L^{-1} solutions of hydrochloric acid from various sources

Acid ID	Container	MeHg (<i>k</i>)	PhHg (<i>k</i>)	diPhHg (<i>k</i>)	Fe	Zn	Si	Al	Ca	Na
5	Brown glass	0.037	0.028	0.035	0.024	0.2058	0.048	n.d.	0.05	0.460
1	Brown glass	0.034	1.4 ^a	1.4 ^a	0.121	0.7566	0.024	0.13	0.23	0.328
4	Translucent plastic	0.005	0.009	0.016	0.029	0.3208	0.023	n.d.	0.06	0.530
2	Translucent plastic	0.001 ^a	–	–	0.037	0.4871	0.018	0.06	n.d.	0.193
3	Black plastic	0.001 ^a	–	–	0.027	0.3949	0.022	n.d.	0.06	0.150

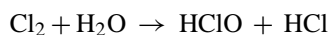
Data are presented in order of decreasing methyl-mercury kinetic constants.

^a *k* Values that were estimated from only 1–2 data points. All other *k* values were calculated from 8–10 data points. K, Cd, and Cu were below their limit of quantification for all acids.

hydrogen in chlorine following the reaction [9,10]:



Concentrated hydrochloric acid contains chlorine and water, which may react giving a mixture of hypochlorous acid and hydrochloric acid:



Suda et al. have demonstrated that the degradation of methyl and ethyl mercury into inorganic mercury by human polymorphonuclear leukocytes was due to the hypochlorous acid produced by such cellules [11]. Thus some experiments with the hypochlorite ion were done.

Results dealing with hypothesis one are shown in Table 2. Fig. 4 shows results dealing with hypothesis two. Degradation constants *k* did not correlate with metal concentrations in the hydrochloric acid reagents (see Table 2). As shown in Fig. 4 the combination of HCl and NaClO plus ultrasonication is the key for a correct degradation of organomercurials.

Table 3 shows the results obtained for degradation of methyl-mercury in the presence of hypochlorite ion. As can be seen, the recovery with acid I was total, which was expected and was aforementioned in this work. Recovery greatly increased to almost 100% when NaClO was added to acids II and III. Thus it was demonstrated that the presence of hypochlorite was critical for the correct degradation

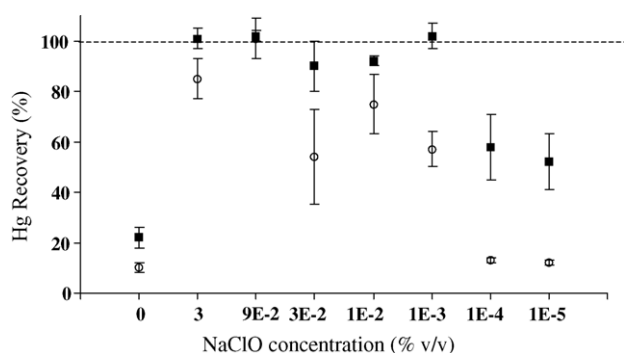


Fig. 4. Degradation of methyl-mercury as a function of NaClO concentration. Conditions: HCl 1M, (○) no ultrasonication, (■) with ultrasonication: 40% amplitude, 10 ml solution, 6 mm probe tip, 60 s sonication time.

Table 3

Degradation of methyl-mercury in the presence of NaClO in different liquid media

Liquid medium ^a	pH	Hg recovery (% , n = 3)	R.S.D. (%)
HCl 1 M + NaClO 3% ^b (v/v)	0.26	100 ± 8	8
HCl 1 M + NaClO 3% ^c (v/v)	0.26	92 ± 7	8
HCl 1 M + NaClO 3% ^d (v/v)	0.26	95 ± 6	6
NaClO ₄ 3% (v/v)	11.6	29 ± 4	14
HNO ₃ 1 M + NaClO 3% (v/v)	0.26	59 ± 7	12

^a Sonication conditions: sonication time 90 s; sonication amplitude 50% (Watts delivered 8).

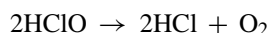
^b HCl was HA I.

^c HCl was HA II.

^d HCl was HA III.

performance, since in the absence of this ion, acid III was not able to decompose the organic-mercurials. Similar results were obtained with acid II. Table 3 also shows that when hypochlorite ion was used alone, the mercury recovered was c.a. 29%. Since the solution of hypochlorite ion is basic, it was possible a lack in the recovery as consequence of an interference in the formation of the vapour mercury in the reactor instead of a lack in the degradation efficiency. Thus, the degradation was also attempted using nitric acid in conjunction with hypochlorite ion, but with the same conditions than with HCl the degradation obtained was 59%. Thus it was clearly demonstrated that only with the presence of HCl plus hypochlorite ion the degradation of the organic mercurials was possible in a reasonable time.

The lower reaction rates obtained for HA II–IV than for HA I and V possibly may be explained by the fact that the hydrochloric acid was packed in translucent plastic and was exposed to light. Hypochlorous acid is known to decompose in sunlight by the following reaction:



4. Conclusions

The fast degradation of organomercurials can be achieved in an HCl liquid medium with the aid of sonication and in

the presence of hypochlorite ion. The degradation rates for methyl-mercury, phenyl-mercury and diphenyl-mercury followed a pseudo-first reaction kinetic. The data reported here demonstrate that sodium hypochlorite added to HCl solutions improves recovery of mercury from organomercurial compounds when mercury is determined by cold vapour-atomic absorption spectrometry using stannous chloride as the reducing agent.

Acknowledgements

J.L. Capelo acknowledges the postdoctoral grant SRFH/BDP/9481/2002 of FCT (Science and Technology Foundation) from Portugal. Professor Dr. Frausto da Silva, Technical University of Lisbon, Portugal, is acknowledged for faithful discussions.

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