Effective UV photolytic decomposition of organic compounds with a low-pressure mercury lamp as pretreatment for voltammetric analysis of trace metals

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Abstract. The effectivity of UV irradiation with low and high pressure mercury (L-Hg and H-Hg) lamps on the decomposition of organic compounds in aqueous solutions, as pretreatment for the voltammetric determination of trace metals, is compared. The photolytic decomposition with the L-Hg lamp was much faster than with the H-Hg lamp. The higher efficiency of the L-Hg lamp is caused by its greater light intensity at short wavelengths. Interferences of organic compounds on the voltammetric determination of nickel and indium were eliminated successfully by ∼ 90 min irradiation with the L-Hg lamp. Humic acid and organic interference with the voltammetric determination of nickel in natural river water were successfully eliminated. The decomposition using the L-Hg lamp can be carried out without added oxidizing reagents and at room temperature, thus eliminating loss of water samples by evaporation at higher temperature.

H-Hg lamp tends to get hot as the power is large (typically 150–1000 W) and water samples are lost by boiling unless efficient air/water cooling is used.

The H-Hg lamp is relatively ineffective for the decomposition of aromatic compounds in part due to side-reactions such as the oxidation of chloride to hypochlorite which rapidly removes the dissolved oxygen which is required for the oxidation of the organic matter [11]. Therefore, chemical oxidizing reagents, such as hydrogen peroxide, which increase the risk of contamination have to be added to accelerate the decomposition rate [10]. The low-pressure mercury lamp, L-Hg, is known to have a line spectrum with a relatively higher fraction at 254 and 185 nm than the H-Hg lamp [13] and more effective decomposition can be expected. However, the L-Hg lamp has not been regularly used. In this paper we compare the effectiveness of a 70 W L-Hg lamp with a 450 W H-Hg lamp for UV-digestion of water at room temperature.

Introduction

Stripping voltammetry has been widely used to measure the low concentration of metal ions in natural waters as no preconcentration step is required even for saline waters. In addition to conventional anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV) with adsorptive collection is very useful [1] to determine metals without the need to reduce to the metallic state, thus preventing the formation of intermetallic compounds.

Organic substances are known to interfere with voltammetric analysis. To decompose these organic substances, conventional decomposition methods, such as heating with acids and oxidizing with bisulfate ion, are inconvenient because the levels of contaminating metals in the reagents are usually high and it is difficult to carry out these procedures in closed systems. Decomposition with UV irradiation by a high-pressure mercury vapour lamp, H-Hg, is frequently used [1–11]. However, the

Experimental

A 70 W L-Hg lamp (Ushio, UL1–70 W, 30 cm length) and a 450 W H-Hg lamp (Ushio, UM 452, 10 cm length) were used. Samples were put in silica tubes (10 mm inner radius and 100 mm long), suspended radially around the lamps at a distance of ca. 2 cm and irradiated under air-cooling with a fan. Ten and four samples could be irradiated simultaneously by the L-Hg and the H-Hg lamp, respectively. Sample temperature during irradiation was $(30 \pm 2.5)\,°C$ for both lamps. Absolute light strength at 254 and 365 nm was measured with a UV powermeter (SEN Lights Co., 306). A spectrophotometer (Hitachi, U-2000) was used for absorption measurements. A voltammetric analyzer (Yanaco, P–1100) and a hanging mercury drop electrode, HMDE, (PAR, 303A) were used for the voltammetric measurements. The reference electrode was Ag/AgCl/3 mol/l KCl. Ni(II) and In(III) were determined by CSV with dimethylglyoxime at pH 9 [14] and ASV at pH 2, respectively. Water samples of river Ina, near Osaka, were collected in acid washed polypropylene bottles and filtered using a 0.22 μm nuclepore filter before measurement.

Results and discussion

The decomposition of several organic compounds as a result of UV irradiation was monitored by spectrophotometry. A number of compounds was selected which are known to behave as surfactants (ionic and non-ionic) as well as compounds known to form complexes (oxine etc). The data were fitted to an equation of the form from which the rate of decomposition, k, and the time to achieve 95% decomposition, t(95%), can be calculated. Values for k and t(95%) are listed in Table 1. The L-Hg lamp was found to be more effective than the H-Hg lamp in the decomposition of all the compounds tested. A likely cause for this effect is the high fraction of shorter wavelength light of the L-Hg lamp. The absolute light strengths measured at 2 cm from the lamps (equal to the distance of the sample tube surface from the lamp) were 35.5 and 3.1 mW/cm^2 at 254 nm, and 10.1 and 3.1 mW/cm^2 at 365 nm for the L-Hg and the H-Hg lamps, respectively (these values showed only little change, ~ 2%, during irradiation for 6 h). The L-Hg lamp was therefore more than 10 times stronger than the H-Hg lamp at 254 nm suggesting that this could be the main reason for the effectiveness of the L-Hg lamp.
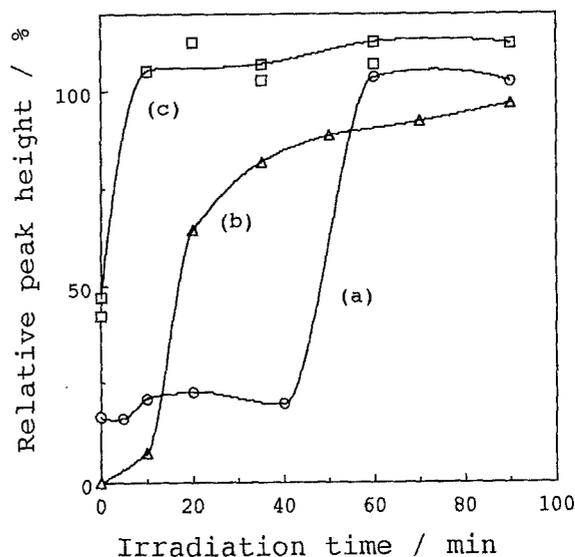
UV irradiation with the L-Hg lamp was applied as pretreatment for the CSV determination of 50 nmol/l nickel. The peak currents were reduced to nearly 20, 0 and 45% of the original value in the presence of 10 mg/l oxine, 12.5 mg/l Triton X-100 and 1 μmol/l EDTA, respectively. UV-irradiation of 60 min (oxine), 90 min (Triton X-100) and 10 min (EDTA) was sufficient to restore the original peaks (Fig. 1). Similar experiments were carried out to evaluate the interference in ASV of 200 nmol/l In(III). The indium peak was almost fully depressed in the presence of 10 mg/l oxine, 12.5 mg/l Triton X-100 and 1 μmol/l EDTA; the interference was removed fully by ca. 90 (oxine), 35 (Triton X-100) and 90 (EDTA) min irradiation (Fig. 2). Therefore, UV-irradiation with a L-Hg lamp is an efficient method to eliminate the interference of organic compounds (surfactants and chelating agents) in ASV and CSV.

Fig. 1. Effect of irradiation time with the L-Hg lamp on Ni (50 nmol/l) peak height with a 10 mg/l oxine, b 12.5 mg/l Triton X-100, c 1 μmol/l EDTA
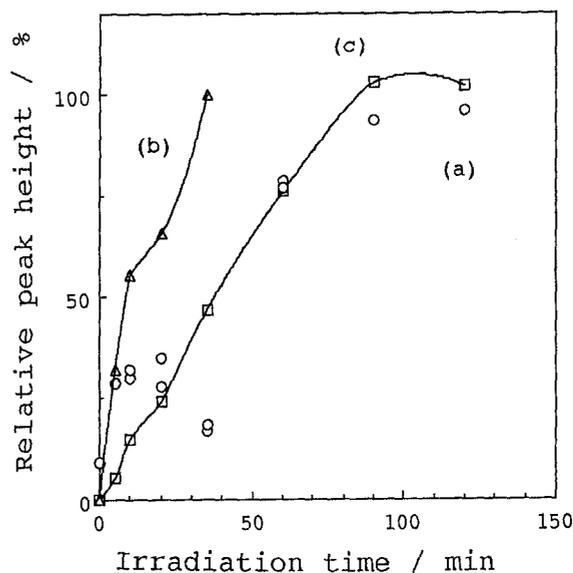
Fig. 2. Effect of irradiation time with the L-Hg lamp on In (200 nmol/l) peak height with a 10 mg/l oxine, b 12.5 mg/l Triton X-100, c 1 μmol/l EDTA

Humic acid was added as a model compound for high-molecular weight organic substances occurring in natural waters. The humic acid caused two types of interference with nickel: it behaved as a ligand by forming a complex with nickel, and as a surfactant by suppressing the sensitivity. Two days after addition of 10 mg/l humic acid to a solution containing 45 nmol/l nickel (pH 7.0) the concentration of reactive nickel was lowered at 38 nmol/l due to coordination with humic acid. The relative sensitivity was 26% lower due to the competitive adsorption of humic acid on the HMDE, reducing the effective electrode area. This solution was irradiated by the L-Hg lamp, causing the complexed nickel to be released and its relative sensitivity to be restored after 2 ~ 4 h irradiation

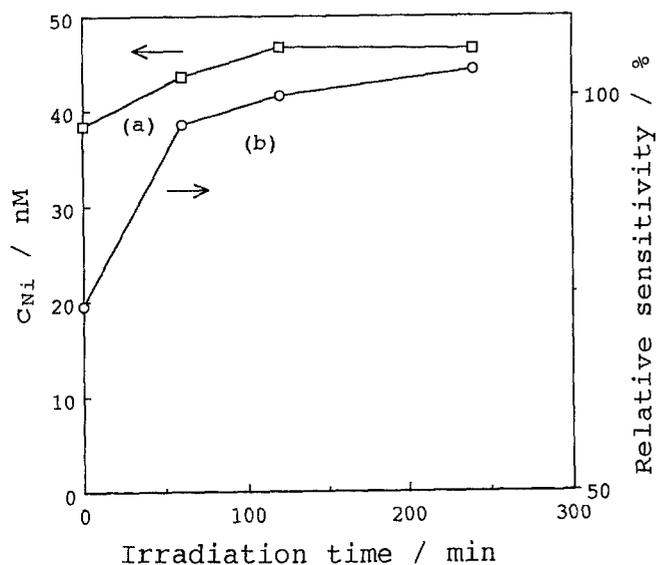**Table 1.** Decomposition rate constants and the time to achieve 95% decomposition

	λ/nm	k/10^{-3} s^{-1} Low	k/10^{-3} s^{-1} High	t(95%)/min Low	t(95%)/min High
Triton X-100	222	3.61	1.78	22	32
SDBS[a]	222	3.47	0.55	14	91
Benzoic acid	223	2.52	0.39	20	129
Salicylic acid	229	4.62	0.68	12	74
Rhodamine B	553	6.30	1.67	8	30
Salicylaldoxime	255	2.68	0.71	19	71
EBT[b]	296	0.46	0.04	109	1119
Salicylaldehyde	210	0.93	0.08	54	603
1-Nitroso-2-naphthol	208	0.57	0.07	87	711
Oxine	235	1.60	0.35	31	143
O-Phenanthroline	222	2.02	0.25	43	335
Fluoresceine	229	1.34	0.15	37	326
Humic acid	260	0.45	0.16	111	320

[a] SDBS; Sodium dodecylbenzenesulfonate
[b] EBT, Eriochrome Black T

Fig. 3. Effect of irradiation time with the L-Hg lamp on Ni concentration and sensitivity with 10 mg/l humic acid; *a* concentration, *b* relative sensitivity

(Fig. 3). The irradiation with the L-Hg lamp was therefore also effective in the destruction of natural organic compounds without addition of any oxidizing reagents.

Nickel in river water was determined before and after 4 h irradiation with L-Hg lamp. The labile and total concentrations were 58.8 ± 0.3 and 75.7 ± 2.5 nmol/l, respectively. This means 22% of the nickel (17 nmol/l) was bound by natural ligands in the river water. Addition of 50 nmol/l nickel to the river water, and CSV analysis after allowing the sample to equilibrate for a day gave labile and total nickel concentrations of 108.1 ± 1.8 (labile) and 126 .0 ± 0.6 nmol/l (total), respectively, indicating full recovery of the added 50 nmol/l nickel. This finding indicates that the added nickel was not complexed by the natural ligands suggesting that the natural ligands were already saturated with nickel. These observations are consistent with data for seawater [15, 16] and rain water [17].

The destruction of other organic compounds, and the application to metal speciation studies, are investigated in our laboratory.

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