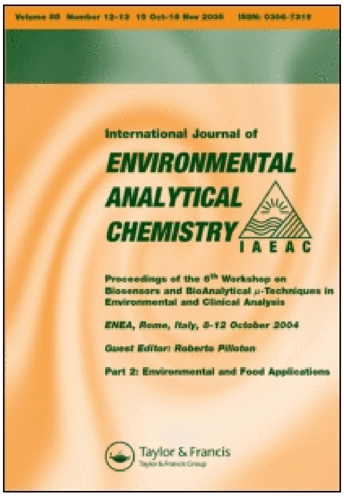

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PRELIMINARY STUDY ON DEGRADATION OF IONIC ALKYLLEAD SPECIES IN WATER

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Laboratory experiments are reported, aimed at monitoring the degradation of ionic alkyllead compounds in water in the dark, in daylight and with UV irradiation. A stepwise dealkylation in aqueous media is not supported by the simulations. It appears that trialkyllead (triAL) degradation does not give rise to appreciable formation of dialkyllead (diAL) but directly yields inorganic lead; on the other hand, dialkyllead species appear too stable to be involved as short-lived intermediates. Generally ethyllead compounds are observed to be more sensitive towards degradation than the corresponding methyllead compounds. The results are consistent with existing literature evidence.

KEY WORDS: Organolead compounds, degradation, water, GC–QFAAS.

INTRODUCTION

Tetraalkyllead (TAL) compounds were introduced in 1923 as gasoline additives to prevent premature ignition (knocking) of the fuel-air mixture in the cylinders of internal combustion engines. In the seventies their manufacture reached approximately 3.5 10^5 tonnes Pb annually. Since 1975 many industrialized countries are making progress in banning the use of lead in gasoline, as required to prevent poisoning of exhaust system catalysts which limit emissions of nitrogen oxides, carbon monoxide and hydrocarbons.

The specific form of the compounds entering the biosphere due to the widespread use of organolead was both expected and found to be largely inorganic, reflecting the relative instability of the alkyllead species[1]. It was recognized, however, that the acute mammalian toxicity of 'organoleads' is from 10 to 100 times greater than that of the inorganic Pb^{2+} ion, and that these organolead species moreover mediate deleterious changes in biological systems which are distinctly different from classical 'plumbism'. Thus, although organoleads may comprise only a small fraction of the total lead burden, they may be anticipated to modify the 'total lead' toxicity appreciably.

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To aid in the interpretation of the alkyllead species composition observed in environmental water, laboratory experiments monitoring transformations in a conditioned sample may yield valuable indications. Though a quantitative extrapolation of these results is probably hampered by many factors, such as interactions with the vessel walls and the absence of transfer processes between different compartments of the biosphere, at least some information on the chemical identity and the fate of the species formed becomes available. Of the fairly detailed studies on the decomposition of alkyllead compounds in aqueous solutions, most were carried out at initial tetraalkyllead concentrations of $>10^4\,\mu g.L^{-1}$ (as Pb), which is many orders of magnitude greater than the amounts encountered in most environmental situations. Only a few years ago, well optimized speciation methodology which is indispensable for more detailed and realistic experiments became available. The mounting concern about the degradation pathways of alkyllead and other organometallic compounds in the environment meanwhile has created a need for intercomparison studies and reliable standard materials.

Our activities in the field of alkyllead degradation have so far consisted mainly of fragmentary experiments, in part carried out and reported elsewhere by Chakraborti *et al.*[2]. Some as yet unpublished results are described below.

EXPERIMENTAL

Reagents

The organolead salts were kindly provided by the Associated Octel Company (R & D Dept., South Wirral, U.K.). The purity of the individual compounds was assessed by gas chromatography-quartz furnace atomic absorption spectrometry (GC–QFAAS) after diethyldithiocarbamate (NaDDTC) extraction and butylation[3,4]. The total lead content of the concentrated aqueous standard solutions was checked periodically by flame or graphite furnace AAS after a classic wet digestion in an erlenmeyer fitted with a condenser, to eliminate the risk of volatilization losses, using suprapure HNO_3 and a $1000\,mg.L^{-1}$ inorganic lead standard (Titrisol 9969, Merck, Darmstadt, Germany) for calibration. Total ionic alkyllead determinations were carried out using a dithizone extraction followed by acidic back-extraction and AAS measurement (modified after Ref. 5). The combination of chromatographic and spectrometric analysis ensured the reliability of the input data for the study.

The use of *n*-butyl derivatives of the organolead halides as calibrants for the determination of ionic alkyllead by GC–QFAAS required the synthesis of four unsymmetrical tetraalkyllead standards of the type PbR_nBu_{4-n} (R = Me or Et, $n = 2$ or 3) in nonane. These were prepared by reacting the organolead halides, dissolved or extracted into nonane, with a 2 M solution of *n*-butyl magnesium chloride in tetrahydrofuran (Alfa Ventron, Karlsruhe, Germany). After removal of the excess Grignard reagent and the tetrahydrofuran, the standards were submitted to a series of independent quantification methods, including wet acid digestion, a dithizone/AAS extraction procedure (after ICl pretreatment) and GC–QFAAS purity assessment, as described above. The nonane standards were stored in glass volumetric flasks in a refrigerator and a working standard (prepared out of them) was used in all further experiments. All reagents were of analytical grade, and the water used was deionized and further purified through a Millipore Milli–Q system.

Determination

To achieve the separation and quantitative determination of the individual ionic alkyllead species, the 'hyphenated' technique gas chromatography-quartz furnace atomic absorption spectrometry (GC-QFAAS) was selected. A simple interface set-up was found to be feasible by introducing the GC effluent, via a heated nickel transfer line, into the quartz atomization furnace, suspended above the burner of the AAS and thus flame heated. The operating parameters, as well as the extraction/derivatization procedure have been described in detail earlier[3,4]. Excellent absolute detection limits of 40–90 pg (as Pb) combined with a reproducibility of 2–4% and a linear range up to 15–30 ng (as Pb) characterized the GC-QFAAS measurement of the butylated ionic alkyllead species. Based on a 0.5 L sample, the extraction and enrichment procedure followed by GC-QFAAS quantification allowed ionic alkyllead concentrations as low as 1.0–2.2 ng.L^{-1} (as Pb) to be detected, with a typical precision of 5–9% coefficient of variation at the 100 ng.L^{-1} (as Pb) level[6].

Preparation of solutions for the degradation study

The aim of this study was to gain insight in the stability of organolead compounds in water samples under different storage conditions: with UV irradiation, in daylight or in the dark. The preliminary character of the study is reflected in that it was not attempted to define (and monitor) strict and reproducible degradation conditions, or to follow an experimental design worked out by a conventional statistical computer package. Therefore quantitative extrapolation of the obtained data should be considered with due care. For the same reason, no elaborate statistical treatment of the data was carried out; where appropriate to our opinion, a statistical interpretation has been included in the Results and discussion section.

Degradation of alkyllead solutions with UV irradiation. In a first series of experiments, solutions of the individual trialkyllead (triAL) salts containing respectively 1500 ng.L^{-1} (as Pb) of $PbMe_3^+$ or 2900 ng.L^{-1} (as Pb) of $PbEt_3^+$ were studied. They were prepared in deionized water, transferred into quartz erlenmeyer flasks and irradiated for various time periods with short UV light (254 nm). The full content of the flasks was then analyzed immediately using the optimized speciation procedure[3,4]; each of the extracts was injected twice into the GC-QFAAS system.

Furthermore, an experiment was set up in which the UV-induced degradation of a tetraethyllead solution could comprehensively be monitored. The compound was added as a spike to deionized water at a relatively high concentration level (1270 μg.L^{-1} as Pb) as a tetrahydrofuran solution, to ensure good miscibility. After irradiation with short UV light exclusively, a twofold pre-extraction with 5 mL of hexane was carried out on the content of the quartz erlenmeyer (60 mL) to separate the remaining tetraethyllead, which was then quantitatively determined by GC-QFAAS after appropriate dilution. A 25 mL portion of the pre-extracted aqueous phase was taken for the ionic alkyllead determination, using the optimized speciation method. A further 25 mL was subjected to wet acid digestion (HNO_3) followed by a total lead measurement with graphite furnace AAS (PE 3030 AAS, HGA 500 furnace, recommended parameters)[7]. The inorganic lead content was calculated by subtracting from this total lead concentration the ionic alkyllead concentration.

Degradation of alkyllead solutions in daylight Though it was anticipated that, for irradiation with daylight, daily fluctuations in cloudiness, direct solar irradiation, temperature, etc. will complicate the degradation pattern, daylight certainly represents a more realistic experimental condition than short-wavelength UV light. Consequently, both a mixture of the trialkyllead species and a mixture of the dialkyllead (diAL) species were exposed to daylight, and the concentration changes and species composition monitored as a function of time. The trialkyllead experiment was carried out by taking subsamples from a quartz erlenmeyer containing about 200 $\mu g.L^{-1}$ (as Pb) of both trimethyl- and triethyllead, and was performed in mostly cloudy weather circumstances. For the similar dialkyllead experiment the input concentration amounted to 440 $\mu g.L^{-1}$ (as Pb) for $PbMe_2^{2+}$ and 700 $\mu g.L^{-1}$ (as Pb) for $PbEt_2^{2+}$.

Degradation of refrigerated alkyllead solutions in the dark Throughout the study, individual standard solutions of the ionic alkyllead compounds were stored in a refrigerator, without any further preservatives or precautions. By preparing a fresh working solution by dilution regularly, and analyzing its content, information on the long-term stability of alkyllead solutions under these conditions became available.

RESULTS AND DISCUSSION

Short literature survey

Convincing evidence indicates that in every environmental matrix tetraalkyllead (TAL) compounds are eventually converted into inorganic lead through trialkyllead salts; dialkyllead salts are likely to be involved as intermediates, at least in the atmospheric transformations. Monoalkyllead salts are apparently too unstable to permit their isolation, but have been supposed to be intermediates, as well, in a final conversion step to inorganic lead[8-11]. Their occasional appearance in gas chromatography-atomic absorption spectrometric determinations, derivatized to the form of mixed tetraalkyllated compounds, can almost certainly be ascribed to a redistribution caused by analytical imperfection[12,13].

TAL compounds may disappear from aqueous systems as a result of both photolytical breakdown and volatilization losses. Generally, the studies agree that the decomposition of TAL in natural water is a rapid process, light-induced and promoted by various cations[14–19]. Even in the dark, all R_4Pb species (R = methyl or ethyl) decomposed completely within 5 days when spiked at the low $\mu g.L^{-1}$ level in environmental water[19]. In ultrapure water, some 30% of the tetramethyllead input was recovered after 15 days, but no tetraethyllead remained. The principal degradation product in all the investigations was found to be trialkyllead, which in turn decomposed further to inorganic lead. Spiking of a mixture of the five TAL species yielded, among other products, dimethylethyllead and methyldiethyllead, which are regularly observed in the aqueous environment[19].

Trialkyllead and dialkyllead species are considerably more stable in the hydrosphere than R_4Pb compounds. In the dark they are particularly persistent and in this way concentrated solutions in ultrapure water can be stored months without major deterioration. Dilute solutions demonstrate a slow degradation, and after prolonged storage, redistribution reactions may give rise to traces of mixed compounds if methyl- and ethyllead species are kept together[20]; the contrary, though, has also been reported[19]. The decomposition reactions are clearly accelerated by solar radiation[14,19] and similarly as for the TAL compounds ethyl species have an inferior stability compared to the related methyl-containing products[14,19,21]. Fitting the obtained data to a first-order rate expression points to a half-life in the order of 1 day for triethyllead and 10 days for trimethyllead[22].

Interestingly, almost all the data indicate that a simple pathway TAL → triAL → diAL → Pb^{2+} does not explain the degradation of alkyllead in an aqueous environment. Except in one study[18], dialkylleads have not been detected, or only in trace amounts, as intermediates in the trialkyllead decomposition. The species themselves, however, appear sufficiently stable[19] to exclude a fast conversion to inorganic lead as suggested in earlier reviews[8,23].

Degradation of alkyllead solutions with UV irradiation

Trialkyllead compounds appear to be fairly stable if protected from direct sunlight. Exposure to normal electric light (at a distance of 50 cm from a 20 W TL-lamp) did not affect the concentration of 0.5 $\mu g.L^{-1}$ (as Pb) trialkyllead solutions, whereas sunlight clearly induced an exponential decrease[24]. Thus it was thought that irradiation with UV light might serve as a means to artificially stimulate the degradation, with the aim of obtaining qualitative insight in the fate of the species under well-controlled conditions and within a limited time period.

The results of the series of experiments with the individual trialkyllead salts are summarized in the plots of Figure 1. The trialkyllead concentration clearly decreases exponentially with time and the species has an inferior stability compared to the analogous methyllead product; in the best fit of the latter, the data points appear rather scattered ($r = -0.931$ for triML, -0.998 for triEL). No detectable concentrations of other alkyllead products were formed as a result of the degradation process.

The possibility was considered that dialkyllead species participate as intermediates in the trialkyllead degradation in water, but that their low stability towards short UV light would prevent their detection in more than minute quantities. Irradiation

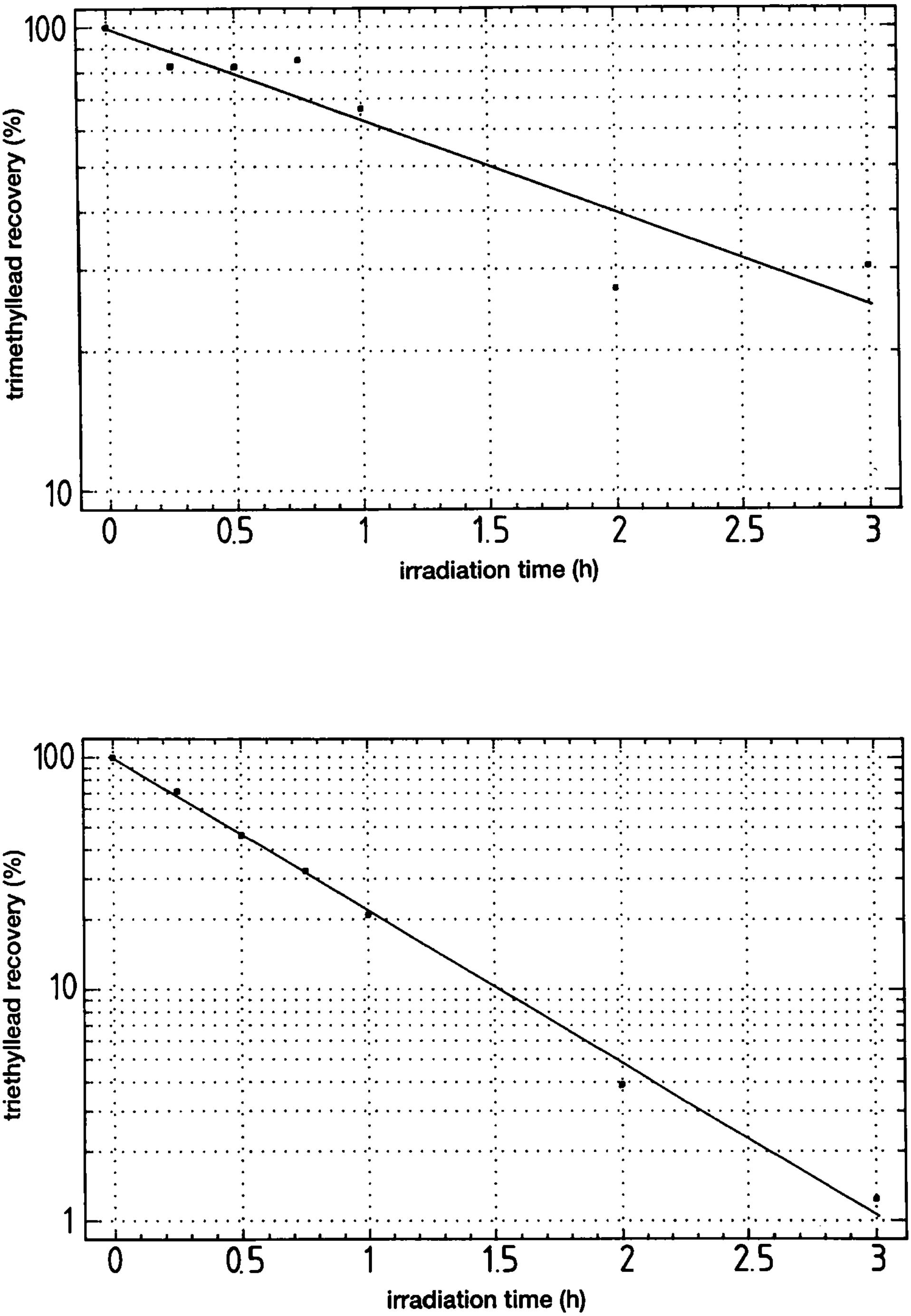


Figure 1 Degradation of a trimethyllead (upper curve) or triethyllead (lower curve) solution irradiated for various time periods with short UV light (254 nm).

of dialkyllead solutions under similar circumstances revealed, however, that a fast degradation cannot explain their apparent absence. After 16 h, about 80 and 50% of dimethyllead and diethyllead, respectively, still remained present; these figures had become 54 to 28%, respectively, after 40 h. Harrison and coworkers, whose daylight irradiation studies pointed to conclusions similar to the above, suggested a direct decomposition to inorganic lead as a breakdown pathway, rather than a successive dealkylation as assumed traditionally[19]. The significant dialkyllead concentrations in environmental water would then probably result from direct deposition of these species after generation in the atmosphere[25]. Interestingly, a direct degradation of tributyltin to monobutyltin in daylight has been observed earlier in organotin stability studies[26].

The results of UV-induced degradation of the tetraethyllead solution are summarized in Figure 2. The concentration of tetraethyllead decreases rapidly and almost exponentially; its half-life is estimated at about 15 min. Triethyllead is initially the principal reaction product detected; it reaches its maximum concentration (45% of the lead input) after about 30 min. Inorganic lead is the final breakdown product, and its contribution to the total lead content of the sample rises gradually; diethyllead formation is limited to less than 2% of the lead input. This seems to confirm the previous findings that dialkyllead hardly plays a role of significance in the degradation of the higher alkylated species.

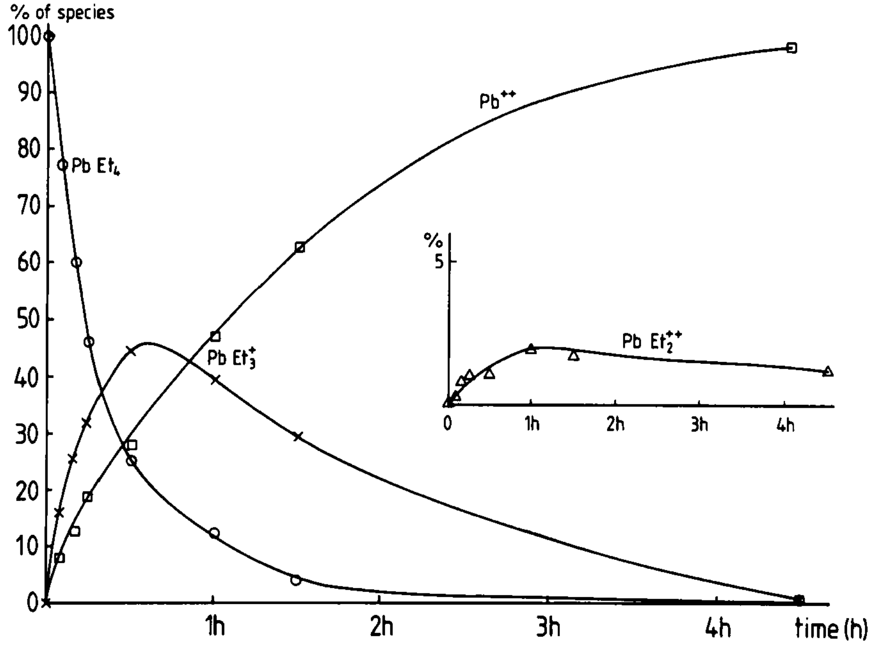


Figure 2 Degradation of a tetraethyllead solution irradiated for various time periods with short UV light (254 nm), and ingrowth of lead-containing breakdown products.

Degradation of alkyllead solutions in daylight

From the plots compiled in Figure 3 it follows that, as expected, the ethyllead compounds are the less stable towards photolytic decomposition. Organolead species other than the reactants were only observed in the trialkyllead degradation; the dialkyllead products detected, however, never exceeded trace concentration levels (up to 3–7% of the trialkyllead spiked).

Earlier it has been noticed that the breakdown of ionic alkyllead species in daylight apparently obeys first-order kinetics[15,19,21,27]. An exponential regression was calculated using the data of Figure 3; highly significant relations were obtained ($p < 0.01$), and the correlation coefficients were situated between -0.95 and -0.99. The first-order reaction decay rates derived from the experiment are presented in Table 1, which also includes constants reported in or estimated from previous laboratory studies[22]. There is increasing evidence that most of the earlier stability studies, carried out at very high initial lead concentrations of 10^4 μg.L^{-1} (as Pb), may have seriously underestimated the degradation of alkyllead in environmental situations. As the exact experimental circumstances largely influence the decay rates, no attempt was made towards a detailed comparison. Generally, the values found in the present study are somewhat higher than the ones obtained by De Jonghe *et al.*[21] or Radojevic and Harrison[15] in similar investigations, but they differ rarely by more than a factor of three.

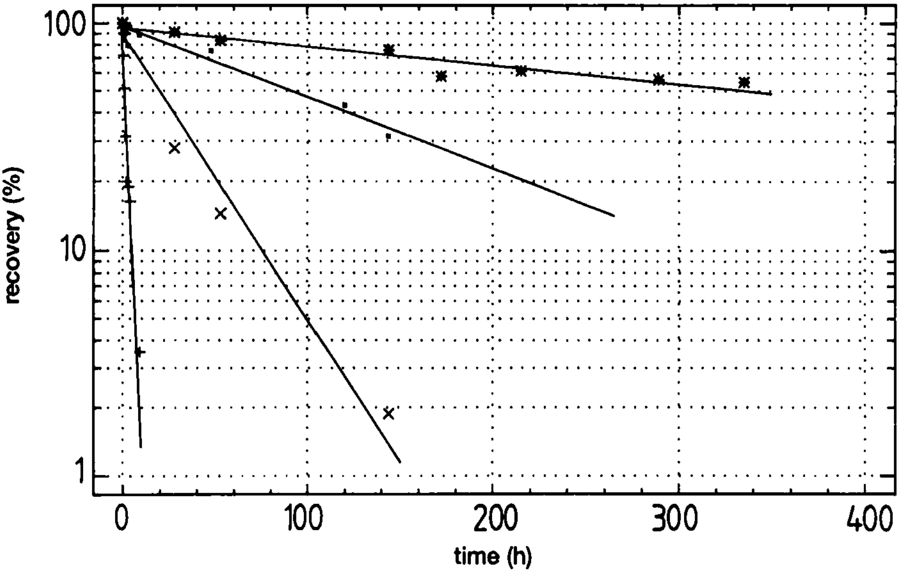


Figure 3 Degradation of tri- and dialkyllead solutions irradiated for various time periods with daylight (O = $PbMe_3^+$, + = $PbEt_3^+$, * = $PbMe_2^{2+}$, X = $PbEt_2^{2+}$).

Table 1 First-order reaction rate constants for the decomposition of PbR_3^+ and PbR_2^{2+} in aqueous samples in daylight

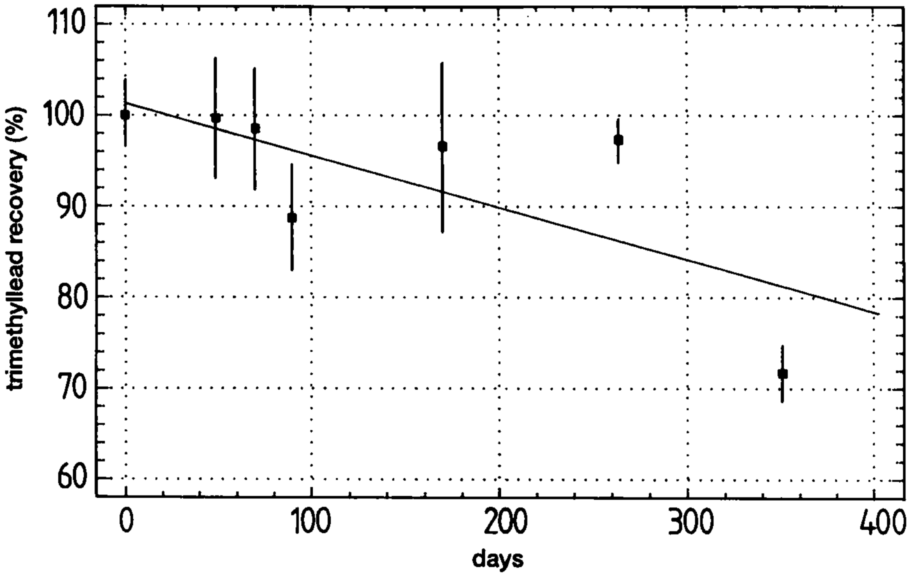
Species	*Reactant conc. ($\mu g.L^{-1}$ Pb)*	*Sample*	*Rate constant k (h^{-1})*	*Reference*[1]
$PbMe_3^+$	0.5	lake water	0.0017	21
	17	rainwater	0.0033	15
	200	deionized water	0.0069	this work
	10000	distilled water	0.0001	14
$PbEt_3^+$	0.5	lake water	0.096	21
	15	rainwater	0.019	15
	200	deionized water	0.29	this work
	10000	distilled water	0.021	14
	10000	distilled water + NaCl	0.0038	27
	10000	seawater	0.0034	27
$PbMe_2^{2+}$	19	rainwater	0.0017	15
	440	deionized water	0.0018	this work
	10000	distilled water	<0.0001	14
$PbEt_2^{2+}$	19	rainwater	0.007	15
	700	deionized water	0.026	this work
	10000	distilled water	<0.001	14
	10000	distilled water + NaCl	0.0029	27
	10000	seawater	0.0047	27

[1] Rate constants based on the experimental data on References 21 and 14 were estimated [22].

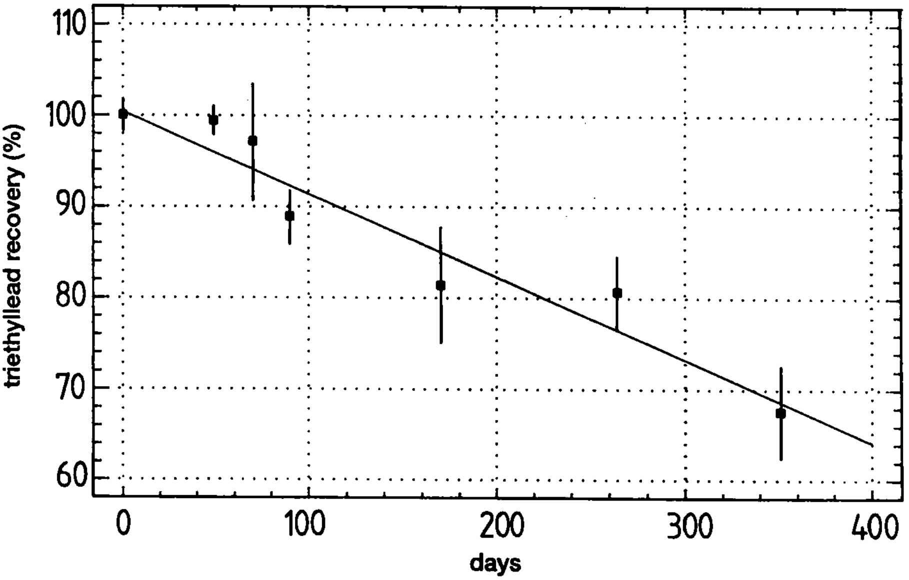
Degradation of refrigerated alkyllead solutions in the dark

Preliminary results after one year of regular monitoring of alkyllead solutions stored in the dark in a refrigerator are summarized in Figure 4. As the data points were deduced under variable experimental conditions and based each on a different number of analyses, an error bar representing one standard deviation on the average has been included. For all species except trimethyllead a clear decomposition could be demonstrated; this occurred always without formation of other ionic alkyllead species.

The ethyllead species were again the most sensitive towards degradation, the loss of triethyllead amounting to about 30% after one year for a 40 ppm solution. The dialkyllead salts used were largely contaminated by decomposition products from the beginning of the experiment; it might therefore be possible that the plots in Figure 4 do not reflect the stability of the pure compounds. For trimethyllead the final data points seemed rather too scattered ($r = 0.72$ whereas for the other species $r > 0.94$) to allow a definite evaluation. It is interesting to note that according to this experiment the trialkylleads would be more stable in the dark than the corresponding dialkyllead species, which is the reverse order of that observed in daylight. Careful reinterpretation of earlier work of Jarvie *et al.*[14] points to the same conclusion. It remains as yet unclear whether a different degradation pathway may explain this remarkable discrepancy.

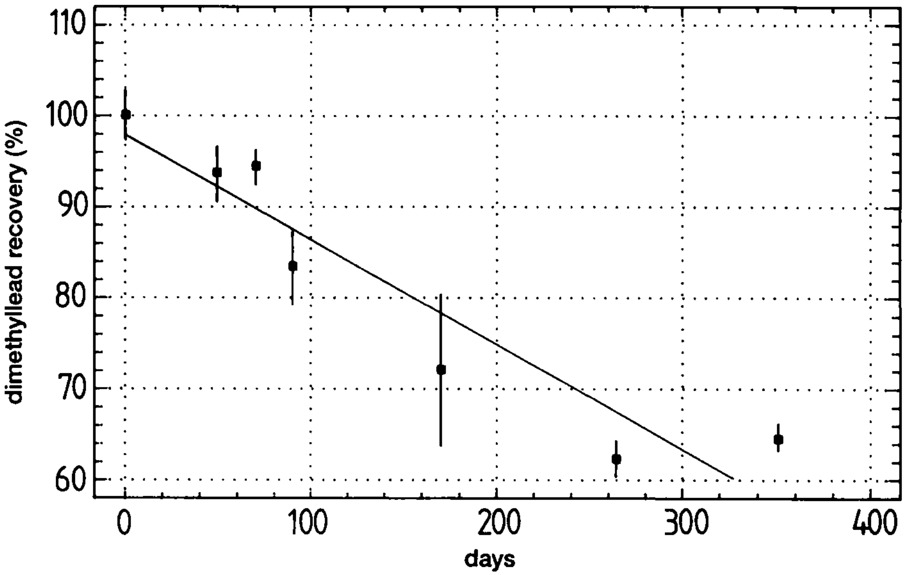


(a)

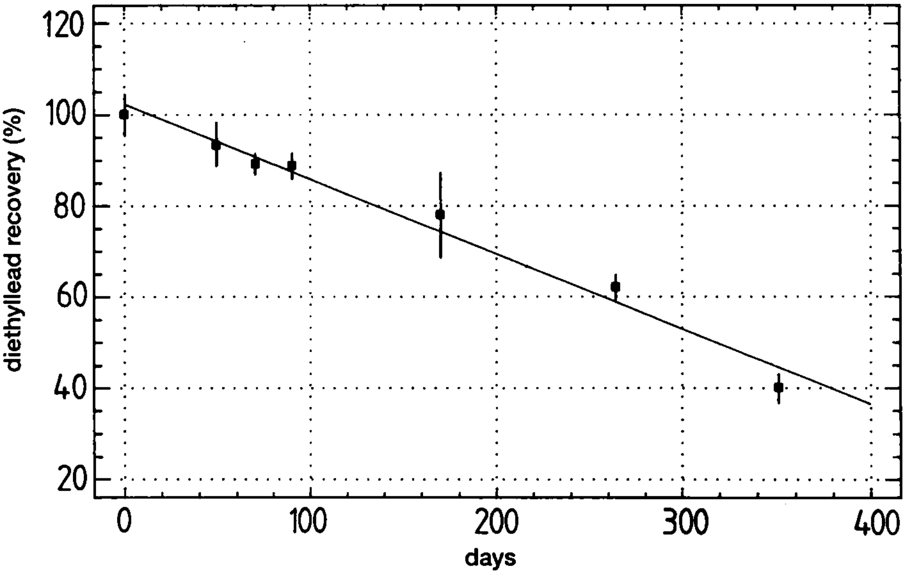


(b)

Figure 4 Degradation of ionic alkyllead stock solutions stored in the dark at 4°C. (a) $PbMe_3^+$ (40 $mg.L^{-1}PbMe_3Cl$); (b) $PbEt_3^+$ (40 $mg.L^{-1}PbEt_3Cl$); (c) $PbMe_2^{2+}$ (198 $mg.L^{-1}PbMe_2Cl_2$); (d) $PbEt_2^{2+}$ (91 $mg.L^{-1}PbEt_2Cl_2$).


dimethyllead recovery (%)
110
100
90
80
70
60
0
100
200
300
400
days

(c)


diethyllead recovery (%)
120
100
80
60
40
20
0
100
200
300
400
days

(d)

CONCLUSIONS

Though it should be stressed that the laboratory experiments reported above are of a fragmentary and preliminary nature, they clearly yield evidence for a degradation of ionic alkyllead which does not follow a stepwise dealkylation pathway. Further and scrutinously planned studies yet remain to be performed before this observation may be extrapolated to the actual environmental process.

With respect to the preparation of 'standard' samples of a sufficient stability for an intercomparison exercise, ionic methyllead compounds are likely to be preferred as analyte, and (at least) storage in the dark may well show to be a prerequisite to minimize unwanted breakdown. In addition, earlier work[6,12,13] has indicated that the possibility of redistribution reactions during sample storage and/or analysis need not to be underestimated.

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