

Automated method
Mercury
Adsorption rates
Particulate matter
Méthode automatisée
Mercure
Vitesses d'adsorption
Matière particulaire

An automated method for the assessment of mercury adsorption rates on particulate suspended matter

W. Baeyens ^a, G. Decadt ^a, F. Dehairs ^{**}, L. Goeyens ^a

^a Laboratorium voor Analytische Scheikunde, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium.

^{*} Senior research assistant at the National Fund for Scientific Research, NFWO-Belgium.

Received 6/11/81, in revised form 11/3/82, accepted 18/3/82.

ABSTRACT

A continuous filtration system connected to a mercury auto-analyzer has been constructed for obtaining mercury adsorption rates on particulate suspended matter. The capabilities of this device have been demonstrated by carrying out a series of experiments under controlled physicochemical parameter conditions on samples of the Scheldt estuary. Duplicate measurements showed coefficients of variation ranging from 1 to 6%. Depending on the physico-chemical conditions, the initial adsorption rate per unit of dissolved mercury concentration varied between 1.2 and $8.1 \times 10^{-2} \text{ min}^{-1}$.

Oceanol. Acta, 1982, 5, 3, 261-264.

RÉSUMÉ

Une méthode automatisée pour la détermination des vitesses d'adsorption du mercure sur la matière en suspension.

Pour obtenir des vitesses d'adsorption du mercure sur la matière en suspension, nous avons construit un système de filtration en continu, branché sur une chaîne d'analyse automatique du mercure. Les performances de ce système ont été évaluées sur une série d'échantillons prélevés dans l'estuaire de l'Escaut et maintenus dans des conditions physico-chimiques rigoureuses. Les coefficients de variation obtenus après une deuxième série de mesures sont compris entre 1 et 6%.

La vitesse d'adsorption initiale par unité de concentration en mercure dissous varie selon les conditions physico-chimiques entre $1, 2$ et $8, 1 \cdot 10^{-2} \text{ mn}^{-1}$.

Oceanol. Acta, 1982, 5, 3, 261-264.

INTRODUCTION

Mercury concentrations currently measured in the North Sea and the Scheldt estuary appeared much lower than those permitted by thermodynamical solid-dissolved equilibrium calculations (Baeyens *et al.*, 1979). The reason that seawater and estuarine water are so depleted in mercury, and according to Turekian (1977) also in several other trace metals, is due to the role particulates play as sequestering agents for these elements (e. g. Bothner, Carpenter, 1972; Lockwood, Chen, 1973; Reimers, Krenkel, 1974; Lindberg, Harriss,

1977; Frenet-Robin, Ottmann, 1977 and 1978). Kinetics are, however, still poorly known. This is mainly due to the fact that adsorption rate measurements require the elaboration of an appropriate experimental device. Indeed, Lockwood and Chen (1973) reported that in many of their runs, the rate was too fast to measure even by the most rapid solids separation methods available. Similar difficulties were encountered by Reimers and Krenkel (1974). They solved the problem by assuming the adsorption rates to be of zero order as a simple approximation.

This work describes an analytical method which allows the automated assessment of adsorption rates. In addition, the influence of some important water-quality parameters such as temperature, salinity, pH and redox potential on the reaction rate can be accurately studied.

APPARATUS

A detailed schematic diagram of the whole analyzing device—a reaction vessel connected to a mercury auto-analyzer through an automatic switching valve—is shown in Figure 1.

Sample is continuously pumped out of the vessel by a Technicon pump, but a Millipore filter fitted in an air-tight filter head at the outlet of the vessel, prevents losses of particulate material. Although a partial clogging of the filter could not be avoided, it appeared that: a) the outlet flow rate remained constant during the time of the experiment; and b) the amount of suspended material in the vessel had not substantially decreased. The solution leaving the reactor is automatically replaced by filtered sample, so that changes in the volume of the reactor sample were avoided.

Through the injection system known amounts of mercury were added to the sample, using an automatic Hamilton syringe (5-20 μ l). Insertion of the thermometer and the Eh-probes into the sample is possible through air-tight silicone joints.

The principle of an auto-analyzing method involves complete return to the baseline between two samples. Therefore a switching valve, which is controlled by a timer, either conducts sample from the reaction vessel to the mercury manifold and a 2 percent nitric acid wash solution to the waste (position 1 on Fig. 1), or the inverse (position 2 on Fig. 1). For our experimental conditions, a wash solution-reaction solution time ratio of 2:1 appeared to be sufficient for a complete return to the baseline.

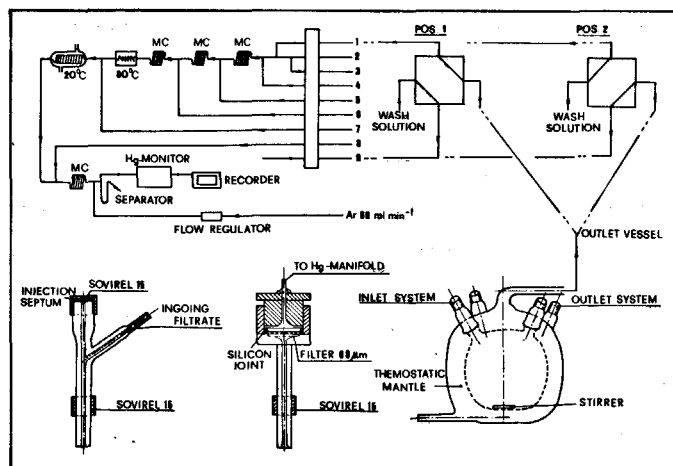


Figure 1

Schematic of system for determination of adsorption rates. 1 = sample, 3.90 ml. min⁻¹; 2 = H₂O, 3.90 ml. min⁻¹; 3 = air, 2.00 ml. min⁻¹; 4 = HNO₃ (1+2), 0.42 ml. min⁻¹; 5 = H₂SO₄ (1+1), 0.42 ml. min⁻¹; 6 = KMnO₄ (1%), 0.10 ml. min⁻¹; 7 = NH₄OCl (1%), 0.23 ml. min⁻¹; 8 = NaBH₄ (1%), 0.10 ml. min⁻¹; 9 = waste, 3.90 ml. min⁻¹. MC = Mixing Coil. POS 1,2 = Position 1,2 of the switching valve.

In the mercury manifold, reactor sample or wash solution is successively acidified with nitric (1+2) and sulphuric acid (1+1), oxidized at 80°C with potassium permanganate (1%) and cooled to 20°C. The excess potassium permanganate is eliminated with hydroxylamine (1%) and mercury (II) is reduced to metallic mercury with sodium tetrahydroborate (1%). In the gas separator metallic mercury is swept from the solution by a current of argon. The argon gas flow rate is kept very constant with a Brooks gas flow regulator (60 ml. min⁻¹). The gasstream was dried over magnesium perchlorate. All mercury detections were made on a Coleman Instrument Hg Analyzer (MAS-50).

The reproducibility and detection limit of the manifold have been assessed. Sextuple analyses of a 10, 20 and 30 μ g. l⁻¹ Hg standard respectively showed a coefficient of variation of 0.71, 0.96 and 1.20%. Three times the standard deviation of a series of ten replicate measurements of a reagent blank signal gave us a detection limit of 1 μ g. l⁻¹ Hg.

PROCEDURE

A differential procedure has been adopted for the determination of the adsorption rates. The first experiment, hereafter called the dilution experiment, is carried out on the filtered sample (pore-size of 0.8 μ m), while the second experiment, hereafter called the adsorption-dilution experiment, is carried out on the unfiltered sample. Filtered sample is used as inlet solution.

After injection of a known amount of mercury (II) chloride or metallic mercury, the evolution of the mercury concentration in the vessel sample is followed during 30 to 40 minutes: the dissolved concentration in real time, the particulate concentration from the law of mass conservation as well as from a control measurement at the end of the experiment. As the dissolved mercury concentration in the vessel sample was always a few orders of magnitude higher than in the inlet solution, the former one is continuously diluted. In the adsorption-dilution experiment however, the combined effect of dilution by the inlet solution and adsorption on particulate matter, enhanced the decrease of the dissolved mercury concentration in the vessel. An example of a dilution and of an adsorption-dilution profile is given in Figure 2.

Since the decrease in mercury in the vessel during the adsorption-dilution experiment equals the sum of the decreases due to adsorption and to dilution, one can write at time t :

$$\left(\frac{dC}{dt}\right)_{\text{vessel}} = \frac{D}{V}(C_i - C_0) + \left(\frac{dC}{dt}\right)_{\text{adsorption}}, \quad (1)$$

with C , C_i and C_0 respectively the mercury concentration in the vessel, the inflowing and the outflowing solution, D the inflowing and outflowing rate of solution and V the vessel volume.

Moreover, the first term in the right handside of equation (1) reduces to " $-kC$ " with $k = D/V$, because:

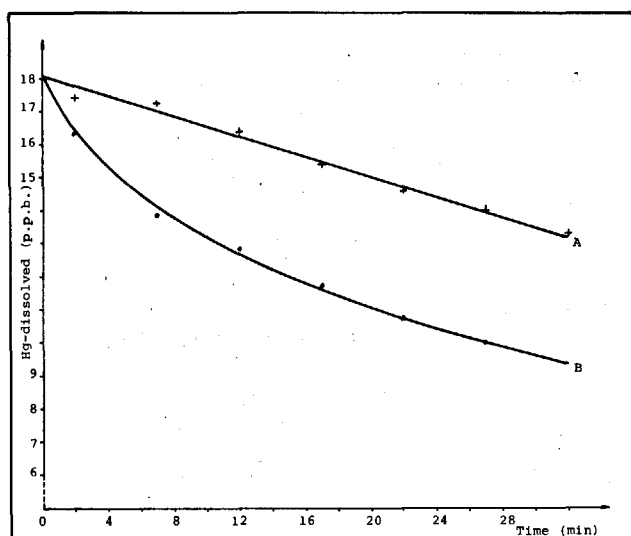


Figure 2
Effect of adsorption on the dissolved Hg-concentration: A) dilution profile; B) adsorption-dilution profile.

a) dye injections showed that the vessel solution is sufficiently homogeneous to admit that C and C_0 are equal, and b) C_i was always a few orders of magnitude smaller than C . An experimental dilution constant k has also been inferred from the obtained dilution profiles. The left handside of equation (1) represents the derivative of the adsorption-dilution curve equation; it has been determined by a least squares polynomial fitting through the set of data-points. It appeared that a cubic curve satisfied very well.

RESULTS

Estuarine samples have been used to demonstrate the capabilities of the method. 30 l of estuarine water were collected in the Scheldt at 90 km from the mouth in October 1976 and April 1977. Initial pH, chlorinity, Eh, turbidity, dissolved and particulate mercury concentrations were 7.5 and 7.4, 0.8 g.l⁻¹ Cl⁻ and 0.3 g.l⁻¹ Cl⁻, 300 and 280 mV, 520 mg.l⁻¹ and 200 mg.l⁻¹, <0.05 µg.l⁻¹ Hg for both samples, 0.26 µg.l⁻¹ Hg and 0.12 µg.l⁻¹ Hg.

Table
Mercury adsorption rates obtained with a pyrex glass and a plexiglass reaction vessel, under similar physico-chemical conditions.

Parameter conditions ^(b)	Plexiglass vessel		Pyrex glass vessel		Differences
	Initial adsorption rate ^(a) (10 ⁻² l.min ⁻¹ .g ⁻¹)	Initial Hg-concentration (µg.l ⁻¹)	Initial adsorption rate ^(a) (10 ⁻² l.min ⁻¹ .g ⁻¹)	Initial Hg-concentration (µg.l ⁻¹)	
Reference			31	18.0	
Reference	27	20.0	29.8 ^(a)	20.0 ^(a)	-2.8
Reference	26.7 ^(a)	22.9 ^(a)	28	22.9	-1.3
Reference	26.3 ^(a)	26.2 ^(a)	28	26.2	-1.7
Reference	26	28.3	27.4 ^(a)	28.3 ^(a)	-1.4
Reference	25	29.0	27.1 ^(a)	29.0 ^(a)	-2.1
Reference	22	42.9	23	42.3	-1
T=40°C	31	29.3	40	24.9	-9
T=14°C	13	29.5	12	34.8	1
+20 g.l ⁻¹ NaCl	15	29.2	15	28.5	0
Eh=150 mV	29	26.3	24	26.4	5

^(a) These values are linear interpolated values. ^(b) Reference: T=25°C; Eh>300 mV; salinity <1.3 g-NaCl.l⁻¹; turbidity=100 mg-solid.l⁻¹ for sample 1 and 260 mg-solid.l⁻¹ for sample 2. ^(c) The adsorption rate is normalized with respect to turbidity and dissolved-Hg concentration.

The coefficient of variation for the initial adsorption rates resulting from duplicate dilution and adsorption-dilution experiments ranged, depending on the physicochemical conditions, from 1 to 6%. The variation on the dilution constant k contributed only slightly to this overall variation. A sensitivity test indicated that a 10% increase of k , which is beyond the observed range of variation, modified the adsorption rate by no more than 0.3%.

The applied differential method theoretically eliminates any contribution to the adsorption rate resulting from possible interactions with the vessel wall. In order to prove this theory, we compared adsorption rate data obtained with a plexiglass and a pyrexglass vessel under similar physicochemical conditions (see Table). In view of the different nature of the two materials it is unlikely that they react with mercury in an identical way. But this also means that if the mean difference between the two data sets equals zero, the nature of the vessel wall has no influence on the adsorption rate determinations. A paired T-test (Dagnelie, 1970) allowed us to accept the hypothesis of equality of both data sets on the 0.05 level. We also could demonstrate that although the adsorption capacity of the suspended material exceeded by far the amounts of mercury added to the samples, the adsorption rate decreased with increasing amount of adsorbed mercury. However, as soon as the ratio Hg-adsorbed: Hg-dissolved, approached a value of 0.3, the rate became constant.

In conclusion, the device described in this paper has been shown to be sufficiently accurate for the assessment of mercury adsorption kinetics on natural suspended matter. These data can be very valuable in studies dealing with transport and fate of mercury in an aquatic environment.

Acknowledgements

The authors thank Dr. P. J. Craig of Leicester Polytechnic and Dr. E. I. Hamilton of NERC/IMER for their comments on the original manuscript and Dr. P. J. Saunders of NERC for supplying valuable information.

REFERENCES

Baeyens W., Decadt G., Elskens I., 1979. A study of the distribution of mercury in the various compartments of the North Sea and Scheldt Estuary ecosystems, *Oceanol. Acta*, 2, 4, 447-457.

Bothner M. H., Carpenter R., 1972. Sorption-desorption reactions of mercury with suspended matter in the Columbia river, IAEA-SM-158/S, Washington, July 1972, 73-87.

Dagnelie P., 1970. *Théorie et méthodes statistiques*, J. Duculot S. A. éd., Gembloux (Belgium), vol. 2, 451 p.

Frenet-Robin M., Ottmann F., 1977. Phénomènes de fixation et désorption du mercure sur la vase en suspension dans l'estuaire de la Loire, *J. Rech. Océanogr.*, 2, 3, 11-20.

Frenet-Robin M., Ottmann F., 1978. Comparative study of the fixation of inorganic mercury on the principal clay minerals and the sediments of the Loire Estuary, *Estuarine Coastal Mar. Sci.*, 7, 425-436.

Lindberg S. E., Harriss R. C., 1977. Release of mercury and organics from resuspended near-shore sediments, *J. Water Pollut. Control Fed.*, 2479-2487.

Lockwood R. A., Chen K. Y., 1973. Adsorption of Hg (II) by hydrous manganese oxides, *Environ. Sci. Technol.*, 7, 11, 1028-1034.

Reimers R. S., Krenkel P. A., 1974. Kinetics of mercury adsorption and desorption in sediments, *J. Water Pollut. Control Fed.*, 352-365.

Turekian K. K., 1977. The fate of metals in the oceans, *Geochim. Cosmochim. Acta*, 41, 1139-1144.