DETERMINATION OF TRACES OF MERCURY

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ABSTRACT

A large number of methods for determining traces of mercury or of its inorganic and organic compounds are reviewed from papers published during the last 15 years. Aspects concerning the sensitivity, selectivity and accuracy of the methods, the influence of various factors on these parameters, and the results obtained after applying these methods for particular determinations in various media are discussed.

INTRODUCTION

Among heavy metals, mercury may be singled out as one of the main pollutants of the environment. The toxicity of mercury and of its inorganic and organic compounds has been well known for a long time, but their study as a major concern for environmental conservation has been taken up mainly since incidents in Japan, Sweden, Iraq, Pakistan, Guatemala and Ghana.

Mercury can be found in the environment mainly bound in sediments or in water suspensions, in air or in living organisms (plankton, molluscs, crustacea, fish, etc.). Literature data show that mercury, under the influence of some environmental factors, undergoes some alkylation reactions, leading to alkylmercury compounds and finally to methyl mercury – the most toxic of the organomercuric compounds /1-8/.

An exact knowledge of the content of mercury and of organomercuric compounds in the environment opens up the possibility of making sound decisions concerning the eradication of the causes that lead to environment contamination with such pollutants. To this end, a diversity of analytical methods has been proposed; most of these fulfill the sensitivity, selectivity and accuracy requirements for this purpose, mainly as a consequence of the interest shown earlier by chemists in determining mercury in various samples.

Bibliographical studies of methods of determining mercury and its compounds have been published periodically; the last of these, due to Chilov /9/, covers the data up to 1974. The reviews published annually in *Analytical Chemistry* often make references to mercury determin-

ations in the environment, but these are relatively scarce /10-13/, their aim being rather to review all the compounds present in the environment. a review was also published on the determination of mercury in organic compounds /14/, covering data published up to 1977.

For these reasons, we cover in this review, as completely as possible, papers related to the determination of mercury by instrumental methods, published during the last 15 years.

SAMPLING AND SAMPLE STORAGE

Loss of mercury from samples could have several causes: volatilization of mercury compounds, reduction of these compounds followed by volatilization of elemental mercury, adsorption on the walls of laboratory vessels, adsorption on various particles from the solution, and embedding in stable chemical compounds or amalgams. Avoiding contamination of the sample with mercury by adsorption of mercury from the laboratory atmosphere, from reagents or from the apparata used is very important /15,16/. Jenne and Avotins /17/ and Chilov /9/ have reviewed the preservation agents used for mercury in water. To prevent mercury losses, it is necessary that the sample contain a strong oxidizing agent and a strong acid. As oxidizing agents, potassium permanganate and dichromate have been widely used. The former is unsuitable for samples with large contents of chlorides, since it is rapidly reduced by the Cl^- ions. Carron and Agemian /18/ showed that a 1% H_2SO_4 + 0.05% $K_2Cr_2O_7$ mixture is a very good long-term preservation agent for mercury solutions with mercury concentrations below the ppb level, especially if the vessels used are made of glass. El-Awady, who studied the storage of dilute mercury solutions /19/, has attained very good results by adding a 0.5% HNO_3 + 0.5% $K_2Cr_2O_7$ mixture to the samples; these results were confirmed in ref. /20/, whereas Walting /21/ advised the use of 10% nitric acid. Bothner and Robertson /22/ noticed an increase of mercury concentration in samples of acidified water stored in polyethylene vessels. This was attributed either to "leaching from the container surfaces or from passage of mercury vapor from the ambient air through the container wall into the solution or from both sources." Feldman /23/ carried out

a study of the storage of dilute solutions with concentrations of ng's or sub-ng levels of mercury per ml of distilled water, using 1% HNO_3 or 0.5 H_2SO_4 + 0.1% $KMnO_4$, 1% HNO_3 + 0.01% $K_2Cr_2O_7$, or 5% HNO_3 + 0.01% $K_2Cr_2O_7$ mixtures, in glass and polyethylene vessels. He finally recommended a 5 vol.% HNO_3 + 0.01% $K_2Cr_2O_7$ mixture, which did not lead to mercury losses in glass vessels even after five months storage; this was confirmed by Christmann and Ingle /24/. Oda and Ingle /25/ advised against using nitric acid and potassium dichromate for preserving dilute solutions of organomercuric compounds, since a rapid conversion of these into inorganic mercury takes place. Rosian and Wai /26/, who carried out a study on mercury loss rate in aqueous solutions, found that this depends on the nature of the vessel, increasing in the order polyethylene, vinyl polychloride, soft glass. They also found that mercury adsorption diminishes as the containers are used repeatedly and becomes negligible for solutions with 1-100 ppb concentrations in 1M perchloric acid if the glass vessel had been previously equilibrated with a mercury solution of similar concentration /27/. Litman *et al.* /28/ found that for dilute solutions, as well as during lyophilization, mercury is rapidly adsorbed on the surface of polyethylene, glass and teflon. They exaplined the mercury loss by a mechanism of reduction of HG^{2+} to Hg^0 and recommended some analytical methods which minimize sample handling. The errors due to losses or contamination during sample manipulation are very important for mercury and particularly for organomercuric compounds /29,30/. Bloom and Cercelius /31/, using extremely pure reagents, proposed some special techniques for manipulating the samples, managing in this way to decrease the blanks and to increase at the same time the reproducibility of determination. Bricker /32/ found that the mercury loss is rapid in natural waters containing ppt levels of mercury, kept in teflon and glass vessels, and concluded that glass is better than teflon for storing analysis samples, since it retains mercury much less on its surface. Studies on mercury losses from samples of treated and untreated water which contain mercury at the ppb level can be found in ref. /33-36/.

METHODS OF ANALYSIS

In what follows, we shall review recent methods of identifying and determining traces of inorganic, organic and total mercury, beginning with optical methods (colorimetry, atomic absorption spectrometry, atomic fluorescence) and continuing with chromatographic ones, which comprise the largest number of papers. We shall also give attention to electrochemical techniques, particularly stripping voltammetry, and some other techniques (neutron activation analysis, flow injection analysis, amalgamation techniques).

Colorimetric methods

The literature mentions several organic compounds which react specifically with mercury and its derivatives. Among these, dithizone is the most widely used even though it is not selective, forming complexes with a large number of other metals. The complex of mercury with dithizone is sensitive to variations in experimental conditions /37/. However, due to its rapidity, fairly good reproducibility and low cost, this method continues to be applied for routine analyses. As a rule, the complexes formed by dithizone with mercury compounds are extracted in benzene and the extinction is read at 625 nm. To eliminate variations due to dithizone concentration during the determination, it was suggested /38/ to measure the extinction at two wavelengths, 625 and 475 nm; this method allowed the determination of 0.1 ppm of organomercury.

Schuller /39/ used an extraction with dithizone to determine $^{203}Hg\text{-}(NO_3)_2$. Carbon tetrachloride may be used as a solvent for dithizone /40/ and some hydrophobic gels /41,42/ or polystyrene beads /43/ can be used as support. Ueno *et al.* /44/ determined mercury with copper dithizonate at pH 1 by measuring the solution absorbance at 507 and 493 nm. The difference between the absorbances measured at these two wavelengths is proportional to the mercury concentration. Ag^+ and Fe^{2+} ions interfere, so that chloride and fluoride ions, respectively, are used to mask them.

To determine organomercuric derivatives, these are extracted with cysteine in benzene and the extract is then transferred to a dithizone-

chloroform solution, where the corresponding dithizonate is obtained.

A comparative study of the performance of mercury determinations with dithizone and a.a.s. /45/ has shown that while the accuracies of these two methods are close, a.a.s. is much more reproducible.

Total mercury in samples of waste waters was determined using di-β-naphthylthiocarbazone and measuring the extinction at 510 nm /46/. It was estimated that 0.02-0.05 ppm of Hg could be determined in this way. A detailed study /47/ that for determining mercury in concentrations higher than 0.9 ppm recommended mono- and dithiosemicarbazones at pH 4.7.

Unlike dithizone, reagents such as sodium dithiocarbamate /48/, ammonium diethyldithiocarbamate /49/ and copper diethyldithiocarbamate /50/ possess long term stability. To determine mercury quantitatively, other, more intricate, sulfur-containing reagents were also used, such as hydrazine carbothioamide 2-[(4-hydroxy-3-methoxyphenyl)methylene], with which mercury gives a yellow complex that absorbs maximally at 402 nm and allows determination of 0.1-9.5 ppm /51/; qualitative determinations were made /52/ with *N*-methylaniline-*N*-carbodithioate at pH 5 + 7.5, which gives a pale green precipitate. Mehra /53/ determined mercury compounds with glyoxal bis(2-mercaptoanyl), using the "ring oven ' technique.

The Hg^{2+} ion reacts very selectively with various triazenic derivatives. From this class of compounds, Cadion A was proposed /54/ for determining Hg^{2+} in the range 0.1-4 ppm and Cadion B in the 0.2-8 ppm range. In these determinations, out of 49 other ions, only Sn^{2+}, BrX, I^-, I^-, MnO_4^-, SCN^-, CN^-, S^{2-} and EDTA interfered. From the same class of compounds, 6-phenyl-2,3-dihydro *as*-triazine-3-thione at pH 6 + 14 /55/ and 1-(*p*-nitrophenyl)-3-(sodium *p'*-phenylsulfonate)-triazene /56/ were also useful. Various compounds of the diazoaminobenzene class were also used /57-59/ with satisfactory results.

Another group of papers considered determination of Hg(II) with xylenol orange /60-63/. In order to increase the sensitivity of the method, the reactions were carried out in the presence of coupling agents to permit formation of ternary complexes. When Amberlit LA-2 in 1:1:3 methanol-1-butanol-chloroform was used; a 3:2:2-type complex was formed, which allows the determination of 0.19-5.5 ppm of mercury /61/. With diphenylguanidine in 1:1 isoamyl alcohol-

chloroform, 0.25-5.8 ppm of Hg(II) can be determined at 590 nm, as in the case of a more complex system, *i.e.* xylenol orange-citric acid-0.4*M* Na_2HPO_4 ≈63/. Ternary complexes were also used in the case of glycine cresol red and bromothymol blue, in the presence of hexamethylenetetramine /64/, or, in the case of phloxine B, in the presence of 1,10-phenanthroline /65/.

Other reagents synthesized and used in the analysis of mercury compounds include *N*-(*p*-chlorophenyl)benzohydroxamic acid (20-400 ppm) /66/, ammonium 4-(2,3-dihydroxy-4-pyridylazo)benzene arsonate (3-8 ppm) /67/, 2-(5-bromo-2-pyridylazo)-5-diethyl-aminophenol (0.4-2.4 ppm) /68/, 1,3-diphenyl-5-(1-phthalazinyl) formazan (0.25-2.5 ppm) /69/ and 1-salicylidene-5-(2-pyridylmethylidene) isothiocarbanahydrazone (0.75 ppm of Hg in pharmaceutical substances) /70/.

An indirect method was proposed by Tirwani and Verwa /71/; it consists of titrating the solution which contains Hg(II) with 2-mercaptopropionic acid against a comparison sample containing the equivalent amount of reagent.

Crystal violet forms a $RHgI_3^-$ complex with HgI_2, which can be extracted from an acidic solution (~ .4*N* H_2SO_4) in benzene. HgI_2 was obtained after mineralizing the samples with $KMnO_4$ and reacting with KI. In this way, 0.4 ppm of mercury could be determined with a standard deviation of 5% /72/.

Total mercury in waste waters was determined by formation of a mixed complex between Hg(II), 1,10-phenanthroline and bromphenol blue or pyrogallol red /73/.

Organic or inorganic compounds of Hg(II) contained in biological samples can also be determined by use of some inorganic reagents which undergo color reactions. For instance, if a compound of Hg(II) is reduced with $SnCl_2$ and then passed over a filter paper soaked with a 10% $CuSO_4$ + KI solution, a colored spot is produced by HgI_2-CuI, and this may be compared with a series of standards /74/. In order to separate and identify the organic and inorganic compounds of mercury, isothiocyanatopentaaquochromium(III), $CrNCS^{2+}$, can be used; it forms polynuclear species with CH_3Hg^+, Hg^{2+} and Hg_2^{2+}, having the $(CrNCS)_nMe^{x+}$ stoichiometry /75/. In the presence of nitroso R salt, Hg(II) reacts with $Fe(CN)_6^{4-}$ and forms a colored complex whose extinction is measured at 720 nm. The method is not very sensitive: it

permits determination of only 40-100 ppm of Hg(II) /76/. In the presence of bromine, the $HgBr_3^-$ anion forms a 1:1 compound with 2-phenylbenzo[8,9]quinolizino[4,5,6,7-fed]phenanthridinylium perchlorate; this is water-soluble and can be extracted in BuOAc /77/. This method was applied for the determination of some organic and inorganic compounds of mercury with a detection limit of 1.5-15 ppm.

Atomic absorption spectrometry (a.a.s.)

(a) The cold vapour atomic absorption (c.v.a.a.) technique

This determination is usually based on the absorption of mercury vapour at 253.7 nm. Although the 184.9 nm line is about 30 times more sensitive, this can only be used if the system had been evacuated of oxygen and other absorbing substances. Most of the methods used for determining mercury in liquid or solid samples can be adapted to determine mercury in air or other gases. Trujillo and Campbell /78/ advanced a "multistage air sampler," which allowed the sequential determination of mercury adsorbed on particles, mercury vapour and organomercuric compounds by retaining them on a filter, on a silver collector and a gold collector, respectively, and by subsequently desorbing and determining them by c.v.a.a. /79/. To determine mercury under field conditions, its retention from a definite volume of air on a passive gold collector (set up as a gold wire grid maintained in air for a definite time) was investigated /80/.

Slemr *et al.* /81/ investigated the influence of temperature, gas flow rate and other factors on the retention of mercury on gold-coated quartz wool, whereas Yashida and Motojima /84/ found the factors that influence the thermal desorption of mercury from this collector. A comparative study /83/ of three mercury adsorbents, *i.e.*, activated charcoal, silver-coated sea sand and gold-coated sea sand, revealed that the latter gives the best results. Activated charcoal also gives good results for the retention of total mercury from air /84/. The suppression of interferences which may occur during mercury determination by c.v.a.a. in vapour phase will be discussed in the next section.

Determination methods based on the thermal treatment of the samples and c.v.a.a. For analyzing some solid or liquid materials with

high organic loading, a thermal treatment (combustion or pyrolysis) is recommended for releasing mercury. In most cases, mercury contained in the resulting vapour was retained on gold /85-90/ or silver /21,91,92/, from which it was thermally desorbed and determined by c.v.a.a. For samples which contain organic matter, interferences due to incomplete combustion of the organic substances may occur, which, together with the resulting water vapour, can condense on the surface of the collector and decrease its retention capacity. Furthermore, during thermal desorption these substances can themselves desorb and give rise to interferences. A double gold trap may solve this problem /85/. O'Gorman *et al.* /85/ compared three different methods for determining mercury in samples of American coal, *i.e.*, (i) pyrolysis followed by double amalgamation on gold and determination by c.v.a.a., (ii) neutron activation, and (iii) combustion, then dissolution of the resulting products and determination by c.v.a.a. Their conclusion was that the double gold amalgamation method is better, since it is more rapid and less expensive than neutron activation analysis. The method which resorts to combustion and dissolution of the products gives poorer results.

Wimberley /86/ and Nicholson /87/ reported somewhat similar devices for determining mercury in rocks, soils and substances with large organic loading, based on heating the samples in oxygen (in the first case) or in air, removal of water from the resulting gases and purification of these gases with adsorbents, followed by retention of mercury on a gold collector, from which it is ultimately thermodesorbed and determined by c.v.a.a. The interference of sulfur was prevented by mixing the sample, before thermal treatment, with sodium carbonate or calcium oxide. These methods are reasonably rapid, but they require frequent replacement of the adsorbents and need to be used carefully when biological samples are examined /93/, because these are sometimes incompletely decomposed. In order to determine the total mercury adsorbed on the surface of particles in air, this was first filtered through a quartz-fiber filter which had been previously pyrolized /94,95/; the interfering substances present in the resulting gases were removed by adsorption on silica gel and alumina, water was retained on magnesium perchlorate, and mercury was collected on gold deposited on sand.

Dumarey *et al.* /95/ pointed out that the use of a catalyst for

oxidizing the interfering substances, *e.g.*, hot copper oxide or silver, as Trujillo and Campbell recommended /78/, leads to unsatisfactory results as far as the removal of the interfering substances is concerned; they recommended the use of silver wool, heated at 400°C, as oxidation catalyst, followed by the use of specific adsorbents, as indicated by Nicholson /87/. Good results were obtained by Siemer and Woodriff /96/, who ensured the complete oxidation of the samples (coal and biological materials) in a flow of oxygen introduced both in front of and behind the combustion region. Water vapour was retained in a condenser, whereas mercury was collected on a graphite tube coated with gold on its inner side, from which it was then desorbed thermally by means of a carbon-rod atomizer and determined by c.v.a.a. To prevent deposition of water and of organic residues on the gold trap, the trap can be heated at 170-200°C; under such conditions, mercury may also be quantitatively retained /88-90/. An apparatus was built /89/ in which the samples are burned at 650-700°C, the unburned organic substances are oxidized on silver wool heated at 400°C and mercury is retained on gold-coated quartz wool, from which it is then desorbed at 500°C and determined by c.v.a.a. In a different version, the gold-coated quartz wool was replaced by silver wool /91/; in this case no adsorbents were needed for purifying the gases after combustion of the samples and the whole cycle of sample processing could be automated. Retention of mercury from the vapour arising after the thermal treatment of samples in acidic potassium permanganate solution was also proposed /15,85,97,98/; in turn, the potassium permanganate solution can be analyzed by reduction and aeration /15,97,98/. Doolan /15/ obtained good results by applying this method to determine mercury in coal; he also examined the factors which affect the sample combustion and the mercury determination.

Watling /99/ pointed out that mercury present in the gases resulting from combusting biological samples in flowing oxygen can be retained in a potassium permanganate solution. Subsequently, mercury is reduced to its elemental state and is concentrated on silver wool, from which it is then desorbed thermally and determined by c.v.a.a. The method can be applied for determining mercury in a variety of biological samples with no preliminary processing. Good results concerning the retention of mercury from the vapours obtained after

treating the samples thermally in flowing oxygen were attained by applying a cold-finger technique with liquid nitrogen /100,101/. Mercury was extracted from the resulting condensate with a solution of 0.6*M* nitric acid, 0.9*M* sulfuric acid and 0.05% $KMnO_4$ ≈100/, or by refluxing with 7*M* nitric acid for one hour in a special instillation /101/. The efficiency of the latter method was checked on biological samples by using ^{203}Hg as tracer; in all cases, more than 96% of the mercury present was recovered.

The Schöniger oxygen flask combustion technique gave very good results in the determination of mercury in biological samples, coal, etc. /101/. For analyzing rocks or soils, these first had to be mixed with combustible materials.

In order to diminish the interferences occurring in the vapour phase during mercury determinations, instrumental methods were devised which compensate for non-atomic absorption produced by other species by splitting the mercury line by the Zeeman effect /103,104/.

Determination methods based on the reduction and aeration of the solutions, followed by c.v.a.a. This method is simple, easy and requires only short determination times, but it can be applied directly only for samples of relatively simple composition, in which no interfering substances occur. For more complex samples, for instance for biological materials, the method requires a preliminary wet digestion or thermal decomposition stage, followed by mercury retention in absorbing solutions, from which it can be released after reduction. Separation of mercury from solution by reduction and aeration was used by Poluektov and Vitkun /105/ and by Hatch and Ott /106/, who reduced mercury with stannous sulfate and then determined it *via* c.v.a.a. by recirculating the mercury vapour in a closed circuit. This circulation technique, which provides a stable signal, presents several advantages /107/ in comparison with non-circulating methods, in which the signal is recorded as a peak. Absorbance of the mercury vapour can be easily determined and samples with larger volumes can be investigated, but the gas circuit can also introduce "memory" effects due to mercury vapour adsorption on the walls; furthermore, these methods resist automation. Methods in which the recorded signal is a peak are more numerous. Although mercury determination based on its reduction to

the elemental state and c.v.a.a. may seem simple, its application is rather difficult because a large number of parameters are involved, which, if not carefully controlled, may lead to large errors. The influence of a large number of variables (*i.e.*, sample volume /108,109/, temperature /108/, gas flow rate /16,110/, nature of the gas /111/, interferences of some substances present in the solution in which the reduction is made /112-116/, nature of the reducing agent /113/, the parameters of the optical cell /16,117-119/, the type of hollow-cathode lamp, and the effect of the conditions in which the calibration curves are drawn /110/ on the height and area of the obtained peak have been investigated. As a result, it was recommended that an acid and an oxidizing agent should be added to solutions in which mercury is to be reduced, to prevent losses before the reduction proper is carried out /108/. It is necessary that the mercury present in the solution diffuse most efficiently into the flowing gas and that the dead volumes be minimized /16/. The peak height increases with the decrease of the volume of the solution in which the reduction is made /16/. The temperature of the solution in which the reduction is made has a weak influence only on the repartition coefficient of mercury between 10-30°C /108/, but it has an appreciable influence on carrying away the mercury vapours for higher temperature values /108,120/.

By improving the working parameters, the detection limit can be dropped from 0.02 ppb to 1 ppt /16/, whereas the absolute detection limit falls from 0.2 ng to 1 pg. The height and shape of the peak due to mercury vapour absorption can also be influenced by the presence of some interfering substances present in the analyzed solution, such as Cl^-, I^- ions /121/, hydroxylamine (used to reduce the permanganate ion) /112,122/, cysteine (added to stabilize the mercury solutions) /109,123/, antifoaming agents /112/, or fish samples incompletely decomposed /124/. In some cases, the interferences can be decreased by measuring the peak area rather than its height. Many mineral salts have no influence upon the mercury vapour absorption, but those that contain the $C_2rO_7^{2-}$, MnO_4^-, $S_2O_3^{2-}$, I^- or S^{2-} ions cause a very significant decrease in the response. Interferences can also occur due to Cu(II), Ni(II), Pb(II) and Ag(I) ions, as shown by Beruth and Vendelbo /116/, in disagreement with Yamamoto *et al.* /125/. Very pronounced interferences may also occur during mercury determination by the

reduction and aeration technique, from some metals such as platinum, gold, palladium and silver, which, at concentrations higher than 1 ppm, strongly decrease the response signal /108,115,126/. Selenium and tellurium may also interfere /116,117,126/. Suddendorf /114/ proved that these interferences do not depend on the amount of selenium or tellurium present in the analyzed sample, but on the amount of these elements present in the reaction vessel before sample introduction; for this reason, the reaction vessel has to be thoroughly cleaned after each determination. By carrying out the reduction in alkaline media, Bartha and Ikrenyi /115/ significantly decreased the interferences due to the noble metals, selenium and tellurium. The interferences due to nickel, lead, copper and silver could be decreased by complexing these metals with EDTA /116/.

In most cases, stannous chloride in acid media was used as the reducing agent, but hydrazine chlorhydrate and ascorbic acid gave equally good results /113,127/. Stannous chloride only reduces mercury present as inorganic mercury. To reduce total mercury in samples, Magos and Clarkson /128/ proposed the use of an alkaline solution of stannous chloride containing cadmium chloride. Another reducing agent frequently used is borohydride /129,130/, which reduces both inorganic and organic mercury species and can therefore be applied for the analysis of undigested biological samples /131/.

In order to increase the sensitivity of the determinations, preconcentration and carrying away of the vapour with flowing air, after mercury reduction, were also proposed. Thus, a liquid nitrogen-cooled trap was used /132/, from which mercury was removed by heating; in this way, 2 ppb of mercury could be determined. Gold collectors were used to the same purpose /31,116/. Kunert *et al.* /113/ investigated comparatively various adsorbents such as thin gold or silver wires, activated charcoal, or gold, silver, platinum and palladium deposited on asbestos. By using such preconcentration techniques, they succeeded in lowering the detection limit by more than one order of magnitude.

Mercury from waters could be concentrated by its action upon some ion exchange resins /107,133,134/, from which it can be desorbed and determined using the reduction and aeration technique. Good results were offered by resins containing dithiocarbamate chelating groups /133,134/. Mercury solubilization can be achieved by decomposing

with nitric acid (in which case a detection limit of 1 ppb could be attained /31/) or by eluting mercury with a solution of thiourea (in which case the separate determination of inorganic and total mercury could be carried out /135/ by reducing the former with an alkaline solution of stannous chloride and the latter with the same solution to which cadmium chloride had been added; the detection limit was of 0.2 ppb). Sanemasa *et al.* /107/ determined mercury at the 5 ppb level by concentrating it on an anionite, which was introduced after filtration in the vessel in which the reduction of mercury with stannous chloride was carried out. The absorbance due to mercury vapour was measured in a gas recirculation system. This method could be easily applied.

Usually, after reduction the mercury vapour is carried away with a gas which is allowed to bubble through the analyzed sample; this flowing gas can also carry a small amount of water, which is then deposited on the windows of the cell. To preclude such drawbacks, Kimberly *et al.* /134/ carried out first a repartition of mercury between the aqueous and gaseous phases (by mechanically stirring the solution after the reducing agent had been introduced), then carried away the mercury vapour (by passing air through a tube placed at a short distance above the solution) and determined mercury by c.v.a.a. In another version of this method, after repartitioning mercury between the two phases, a definite volume of liquid was introduced to the reduction vessel; this displaced the mercury vapour toward the measuring cell, which gave a stable signal /136/. This method does not require the use of absorbents or pumps for circulating the gas; the apparatus is extremely simple and the detection limit was *ca.* 80 ppb.

Stationary apparata for determining mercury by c.v.a.a. in aqueous or vegetal samples /137-139/ or in undigested fish samples /140-141/ were also proposed. The vessel containing the analyzed sample was connected by a very short tube to the spectrometer cell. Under equilibrium conditions, the vapour absorption remained constant. By means of a hydrogen lamp, a correction of the non-atomic absorption could be made.

To determine mercury continuously by c.v.a.a., continuous-flow cells were proposed /142/, in which the mercury vapours were carried away from a thin liquid layer with flowing air. Continuous-flow cells for determining mercury in water after electrodeposition /143/ and

cells designed for the separation of mercury from aqueous phases by diffusion through a teflon membrane were also built for use in the flow injection method /144/.

Determination of mercury after sample digestion, by the reduction and aeration technique and c.v.a.a. The wet decomposition of organic substances contained in samples, without mercury losses, is a difficult operation owing to temperature restrictions imposed by the volatility of mercury and some of its compounds /145/. Usually, the sample is digested in acidic and oxidizing media /145/, very often with potassium permanganate in sulfuric acid medium. A study was carried out on four methods of determining mercury in fish, i.e., (i) digestion of samples with nitric acid and sulfuric acid, followed by spectrophotometric determination with dithizone, (ii) a similar digestion followed by reduction with stannous chloride and determination by c.v.a.a., (iii) digestion with hydrogen peroxide, sulfuric acid and potassium permanganate, followed by determination by c.v.a.a., and (iv) homogenization and dissolution in sodium hydroxide solution and reduction with a stannous chloride-cadmium chloride mixture. These methods are adequate for determining total mercury in fish, at concentration levels of 0.2 ppm.

Szakacs *et al.* 147/ used a hydrochloric acid-potassium permanganate mixture and bromine monochloride to digest and decompose some organomercuric compounds in water. Both methods were satisfactory, but that using bromine monochloride had some advantages, e.g., a low blank, a detection limit lower than 0.06 ppb and a simpler working procedure. Oxidation of the organomercuric compounds with bromine generated by a bromate-bromide mixture in acid media was described by Forey *et al.* /148, 149/; it also has the advantages mentioned above. To determine total mercury in waters, James *et al.* 150/ treated them with potassium persulfate in a closed tube at 120°C, then reduced mercury with stannous chloride. Relatively small amounts (500 ppm) of chloride interfered in the determinations.

Potassium persulfate /145/, hydrogen peroxide /145/ and perchloric acid /23,145/151/ were used to digest some more complex samples. Digestion with nitric and sulfuric acids was also frequently used /149,152/. To digest fish samples, nitric acid-sulfuric acid mixtures

containing vanadium pentoxide were used /153/. Kaiser *et al.* /154/ recommended to digest the samples with a nitric acid-chloric acid mixture, in an open, long-necked vessel. Under such conditions, no mercury losses could be detected. Welz and Melcher /155/ compared three methods of digesting some marine biological tissues: (i) digestion with nitric acid at 140°C in closed PTFE vessels, (ii) digestion with sulfuric acid-perchloric acid mixtures at 310°C in open vessels, and (iii) combustion in oxygen, condensation of the products and refluxing of the condensate with 65% nitric acid. Methods (i) and (iii) gave the best results, since they did not lead to mercury losses, whereas method (ii) led to losses. To digest some fish samples, their heat treatment in open vessels, with nitric acid-sulfuric acid-hydrochloric acid mixtures, was proposed /156,157/. Contradicting older data, the authors proved that these methods do not cause mercury losses.

Oxidation of organic substances in aqueous solutions was also carried out by circulation of ozone-enriched oxygen /158/ or by photochemical irradiation with UV light /159,160/. Total decomposition of the organomercuric compounds took an irradiation time of about 20 minutes and the method has the sensible advantage of not using reagents for digestion, which might contaminate the analyzed sample. An automated method for determining mercury in waters, using this digestion method, was also proposed /160/; it does not introduce interfering ions into the system such as chloride, present in some digestion reagents.

A detailed comparative study of several methods of digesting the samples and of mercury determination by c.v.a.a. was published recently /20/.

The differential determination of mercury found as inorganic and organic mercury compounds by reduction and aeration techniques and by c.v.a.a. Inorganic mercury can be determined selectively in analyzed samples by reduction with stannous chloride, which does not reduce organomercuric compounds. The latter are then frequently estimated by difference, after determining total mercury, a method which is often inaccurate, especially if the amount of inorganic mercury is large. Total mercury is determined after treating the samples thermally, by wet digestion or by UV irradiation, which convert the organomercuric

compounds into inorganic mercury, or by using energetic reducing agents such as sodium borohydride or stannous chloride in alkaline media, to which cadmium chloride /161/ or a copper salt /162/ had been added. Goulden and Anthony proposed an automated apparatus many years ago for determining separately mercury-containing species, based on the reduction of inorganic mercury with hydroxylamine and EDTA in alkaline media, of arylmercuric compounds and of inorganic mercury with EDTA and stannous chloride, and of total mercury with stannous chloride and cadmium chloride in alkaline media. The detection limit was of 1 ppb Hg for all forms in which mercury can be found. A differential determination of organomercuric compounds can also be made by changing the gas with which the mercury vapours formed during reduction with stannous chloride are carried away. Carrying the vapours with air or oxygen in alkaline media, releases mercury from ethylmercury but not from methylmercury, whereas bubbling with nitrogen releases only inorganic mercury /163/. A series of organomercuric compounds can also be differentiated by using cysteine as complexing agent or by selective reduction methods /164/. Baltisberger and Knudson /75/ proposed a simple differential method of determining total and inorganic mercury from waters by treating the samples with hydrogen peroxide and a small amount of stannous chloride introduced directly in the syringe in which the sample was collected. Under these conditions, organomercuric compounds were totally converted to inorganic mercury.

In similar samples, inorganic mercury and the organomercuric compounds could also be determined by sequential reduction with stannous chloride and sodium borohydride /25,165/. Automated apparatus was built for determining inorganic and total mercury in urine and blood, involving no sample digestion and using the Magos reagent /166/, or in waters after digestion with oxidizing agents /167/. Apparatus was also constructed to perform the sample digestion and mercury determination continuously in waste waters, with a detection limit of 0.1 ppb /168/. A cell for the continuous reduction of various compounds of mercury after these had been separated by liquid chromatography was designed /169/. Organomercuric compounds could be determined relatively exactly by this method if they were first separated from the analyzed sample by distillation, extraction or

chromatography, then converted into inorganic mercury, which in turn was determined by c.v.a.a.

Methylmercury present in fish samples was determined /170/ by its extraction in toluene and re-extraction in aqueous phase, oxidation to inorganic mercury and finally determination by c.v.a.a. Separation of methylmercury from fish samples was also carried out successfully by distillation /168,171/. After distillation, the compound was extracted from the aqueous phase with dithizone, the dithizonate was separated by t.l.c. and then decomposed thermally; the resulting mercury was determined by c.v.a.a. The method is somewhat tedious but is practically free from interferences.

(b) The hot vapour atomic absorption technique

The traditional technique of determining mercury by atomic absorption with hot vapour has only limited application owing to the large losses which usually occur during the pre-atomization stages in the graphite furnace. The thermal stability of mercury was increased by adding potassium dichromate to a solution of the sample in nitric acid /172/, by adding ammonium sulfide and thus forming mercury sulfide /173/, or by forming amalgams with gold /174,175/ in a gold-plated graphite furnace. Concentration of mercury on an ion exchanger which is thereafter processed in the graphic furnace was also used /176/.

The most efficient procedure for preventing mercury losses seems to be that which used hydrochloric acid-hydrogen peroxide or nitric acid-hydrochloric acid-hydrogen peroxide mixtures /177-179/. In a detailed study of thermal stabilization agents for mercury, Lendero and Krivan /180/ confirmed the very good results obtained by using hydrochloric acid and hydrogen peroxide.

Atomic fluorescence

The literature mentions several mercury determinations by non-dispersive atomic fluorescence methods /181-185/, which have been preferred over the dispersive methods. The determinations were usually made after a preliminary step of separating mercury, either by electrolysis on a gold electrode /182/, or after mercury had been

reduced and the vapour carried away with flowing air /184,185/. Covelli and Rossi /186/ made use of a windowless fluorescence cell provided with a gas-shielding system with the aim of reducing fluorescence quenching of the excited atoms, which is mostly caused by atmospheric oxygen. A comparative study/187/ of atomic fluorescence spectrometry and a.a.s. pointd out that atomic fluorescence is more sensitive and gives a wider linear range on the calibration curve. The detection limits so obtained were at the level of a few tenths of pg's.

Chromatographic methods

Chromatographic methods are extremely useful for analyzing mercury compounds in the environment, since they permit them to be determined in various biological, inorganic or organic matrices and to distinguish the mercury species and determine them individually.

(a) Gas chromatography (g.c.)

Among chromatographic methods, the most used today for analyzing mercury compounds is that based on a procedure proposed by Westöö 188/. In principle, this method consists of forming a water-soluble compound from an organomercuric compound and cysteine, extracting the complex with water, acidifying and finally reacting the so formed *R*Hg*X* compound with an aromatic solvent (usually benzene). The organomercuric derivative is determined with a gas chromatograph provided with an electron-capture detector. Later, complexation with cysteine was replaced with preparation of arylmercuric derivatives, both from inorganic and organic species, based on Peters' reaction /189,190/. By using Peters' reaction and a liquid scintillation spectrometer as detector, mercury was determined at the 1 ppb level /190,191/. A well worked out procedure, which permits the extraction and determination of organomercuric derivatives in fish and which could be easily extended to other cases, was proposed by Schafer *et al.* /192/.

The electron-capture detector has been the most used analysis system /193-197/. A standardized method, proposed by the *Analytical Methods Committee* /198/ uses a ^{63}Ni-electron-capture detector for determining methylmercury. The working temperature of the detector

was maintained at 285°C. Despite the risk of "poisoning" the detector foil with organomercuric compounds, the detector temperature must generally be above 180°C. If one worked at lower temperature, this risk would disappear, but the analysis efficiency would be very low indeed. The electron-capture detector also has several other drawbacks: it has poor selectivity, which leads to the necessity of carrying out more than one separation and, hence, to longer analysis times; generally, polar solvents cannot be used, and those which can must be very pure and available in large quantities. For these reasons, other detection systems have also been sought; among the most frequently used, microwave discharge spectrometers (operated at 100 W, 2450 MHz) may be mentioned /199-206/. A greatly improved variant of this detector used today is the atmospheric pressure helium microwave-induced plasma emission spectrometer /207-209/, which permits 0.09 ppm of CH_3HgCl, 0.12 ppm of C_2H_5HgCl and 0.4 ppm of $(CH_3)_2Hg$ to be determined in a mixture /210/. Ballantine and Zoller /211/ used an argon plasma microwave detector to determine methylmercury chloride and dimethylmercury. The absolute detection limit was of 0.05 ng.

Other detection systems, namely atomic absorption spectrometers /212-214/ and mass spectrometers /215-218/ were also coupled to the gas chromatograph. In order to set up the optimum working conditions, various parameters were varied, particularly the type of column filling and its influence. Various packings were used, such as 5% diethyleneglycol adipate on Chromosorb W /189/, diethyleneglycol succinate on Chromosorb W /203,215,219,220/, 5% Carbowax 20M /204/ or polyoxyethyleneglycol on a silanized support /205/. Davis and Sandra /221/ carried out complete combustion of mercury compounds in a quartz capillary coupled to a chromatograph through a column packed with Superox 20M; they detected 100 pg of total mercury.

An efficient way of analysis was described by Callum *et al.* 222/, who resorted to "tearing" methylmercury from animal tissue with the help of an enzyme, followed by gas-chromatographic extraction and determination with an electron-capture detector.

A thorough scrutiny of the working parameters allowed an adequate method to be set up for analyzing total mercury /223/ or mercury in organomercuric derivatives /224/.

(b) Liquid chromatography (l.c.)

This technique has been rarely used for determining mercury, even though recent improvements (particularly h.p.l.c.) have converted it in the meantime into a very advantageous method. MacCrehan and Durst /225/ determined 1 ppm Hg in biological samples by using l.c. coupled with a detector based on a mercury-amalgamated gold electrode. Some details on the apparatus have been mentioned earlier /226/. 2-Mercapto-ethanol was used as a strong complexing agent, which permitted efficient elution of the compounds.

To separate inorganic and organic mercury compounds directly, a double column containing substances with iminoacetate groups (which retain inorganic mercury selectively) and dinitrocarbamate groups (which retain organically-bonded mercury) was used /227,228/. Elution was carried out in the presence of HCl, after which the column was dried at 110°C. Extraction of dinitrocarbamate-organomercuric derivative could be made either with oxygenated organic solvents (e.g., methylisobutyl ketone) or with chlorine-containing solvents (e.g., $CHCl_3$, CCl_4), from which mercury could be extracted with nitric acid and determined from the acidic extract /230-234/. Lo *et al.* 235/ used complexes of various metals with diethyldithiocarbamate to re-extract mercury. By using copper diethyldithiocarbamate, Smejkal *et al.* 236/ succeeded in separating Hg(II) from aqueous solutions; mercury was thereafter determined by a.a.s. at a 0.1-1 ppb level, with a relative error of 4.2-5.2%. Mercury (II) and methylmercuric derivatives were determined separately at pH 9.7 (with a borate buffer) by extraction with diethyldithiocarbamate in $CHCl_3$ on a Hypersol RP-18 column /237/. Mercury was eluted from a dithiocarbamate column with thiourea /135,238/, after which it was determined by a.a.s. Formation of dithiocarbamate complexes was also used to set up an automated system for the determination of several toxic metals, mercury included /239/.

Organic and inorganic compounds of mercury have been lately more frequently determined by h.p.l.c. For this purpose, the mercury compounds can be extracted as dithiocarbamates /240/, dithizonates /241/ or alkanothiolates /242/, with sodium diethyldithiocarbamate in a 7:2:1 methanol-water-$CHCl_3$ mixture /243/ and with silver diethyl-

dithiocarbamate; such methods allow the determination of organic as well as inorganic mercury /244/.

After separating mercury compounds by h.p.l.c., they were detected by several means: flame atomic absorption /245/, inductively-coupled plasma spectrometry /246/, graphite furnace a.a.s. /247,248/, electrochemical detectors /225,249/ or UV absorption spectrometry /250-252/. Recently, the possibility of coupling a h.p.l.c. separation system with the c.v.a.a. spectrometer was investigated /142,253,254/ and it was found that the sensitivity could be greatly increased (down to 0.02 ppm). Such a coupling is, however, difficult, because c.v.a.a. is only able to determine mercury discontinuously whilst h.p.l.c. is a continuous process. For this reason, a special reaction vessel was devised /142/ whih permitted linking of the systems. Use of h.p.l.c. allowed methylmercuric derivatives present in biotic media to be determined separately /255/.

(c) Thin-layer chromatography (t.l.c.)

This method has been relatively little used for quantitative determinations of mercury compounds. It allows nonetheless satisfactory separation and determination of those mercury compounds which have large molecules, particularly organomercuric compounds. Critical difficulties also occur in the case of ethyl- and methylmercuric compounds, which often remain at the start. However, by coupling this method with quantitative determination by a.a.s., some authors /256/ found that 0.023 ppm of organomercuric compounds or 0.007 ppm of total mercury could be determined. Torres *et al.* /257/ determined $Hg(CH_3)_2$ in fish at the 1.7 ppm level by extraction with toluene, whereas Stary /258/ determined 0.01 ppb of organomercuric derivatives by extraction with dithizone. Extraction with dithizone was also used by other authors /259-261/. Other compounds were also used as complexing agents: 2-mercaptobenzthiazol on silica gel /262/, dithiocaramate on silica gel /263/ and silica gel alone /264,265/. A qualitative determination method permits direct location of the complexes of Hg(II) with *p*-diethylaminoarylphenylglyoxal by reacting them with starch on the chromatographic plate /266/267/.

A more recent method of separating organic and inorganic compounds of mercury is high-performance t.l.c., proposed by Bruno *et al.* 268/;

mercury compounds were separated as dithizonates by densitometric means. Up to 85-98% of mercury and alkylmercuric compounds were recovered and the detection limit was of 4 ppm.

In order to detect the presence of mercury rapidly in various media, especially in the atmosphere, an identification method using paper soaked with cuprous iodide was proposed /269/. Although the nature of the reaction of mercury with cuprous iodide has not been elucidated, it is specific and no interferences occur.

The ability of metals such as Hg, Cu or Cd to inhibit some enzymes (e.g., succinate dehydrogenases) has permitted the determination of mercury compounds /271/ by t.l.c.

Electrochemical mthods

(a) Potentiometry

Several potentiometric titration methods were devised to determine total mercury, but they are restricted to relatively high mercury concentrations (above 0.05 ppm) and are affected by interferences /272-275/. After the introduction of ion-selective electrodes, several were proposed for determining mercury. An early attempt was made by Overman /276/, who proposed an iodide-based ion-selective eletrode and obtained a detection limit of 10 ppb, but interfering substances (Fe^{3+} ions, peroxides and various chelating agents) had to be removed from the sample. Interference of Fe^{3+} in the mercury determination with this electrode was also examined by other authors /277/. Based on similar principles, other types of electrode were proposed, either in the liquid /278/ or solid state /279-280/, but these are still not commercially available.

Because the Ag^+ and Hg^{2+} ions contained in Ag_2HgI_4 have considerable mobilities, this compound was used to make ion-selective electrodes with reproducible response to Ag^+, Hg^{2+} and I^- ions /280/. To determine mercury, Sekerka and Lechner /281-284/ prepared and characterized a series of electrodes based on Ag_2HgI_4 and Ag_2HgI_4-Ag_2S precipitates. These electrodes had a Nernstian response down to about $10^{-7}M$ for Ag^+, Hg_2^{2+} and Hg^{2+} ions. The Ag_2HgI_4-based electrode deteriorated quickly, but that based on Ag_2HgI_4-Ag_2S didnot cause problems concerning its mechanical resistance. The latter electrode

could also be used for determining organomercuric compounds, after these had been decomposed with strong oxidizing agents and the interfering ions (Cl^-, Br^-, SCN^-, S^{2-}) had been removed.

For routine determinations, use of a simpler electrode, based on HgS-AgS /285/ or on iodide /286/ and allowing mercury determination at the 0.01 ppm level, was recommended. Several workers /287-289/ used dithiooxamide to titrate mercury potentiometrically. For rapid determinations, a semiautomatic system using a chloramine T-H^2O^2-based ion-selective electrode was derived /290/.

Lately, use of some enzymic systems has shown great attraction for laboratory analytical determinations, because traces or ultratraces of some metals can inhibit their reactions. Attempts were made to build an electrode based on urease, which was useful for determining Hg^{2+} ions down to concentrations of the order of $4 \times 10^{-9} M$ /291/. The method has, however, a major drawback: it requires special working conditions not readily accessible in ordinary laboratories to achieve stability.

(b) Amperometry

Amperometric titrations, though economic and rapid have been, and still are, rarely used for determining mercury and its compounds. Like potentiometric titrations, they are only suitable for determining total mercury. Attempts were made to titrate mercury amperometrically with dinitrilotetraacetic acid, using a rotating platinum electrode, but the method turned out to be only moderately sensitive; for this reason, an alternative was proposed, in which mercury was determined in organomercuric compounds by using bis(2-hydroxyethyl) dithiocarbamate in isopropanol as titrant /292/. For very low concentrations, mercury was titrated with sulphide /293/. A working variant which is very useful for determining mercury amperometrically at the 5 ppb level was proposed by Nygaard /294/ and by Gifford and Bruckenstein /295/. The essential part of their device is a gold electrode, treated to become hydrophobic and yet remain permeable to gases. The element to be analyzed (the method was initially designed for Cd, Hg and Pb) is converted into a volatile electroactive compound, which is then carried by an inert gas over the gold electrode.

(c) Polarographic and stripping voltammetry techniques

The literature reports relatively few analytical methods that satisfy the sensitivity and selectivity requirements imposed by low or very low (10^{-5} – $10^{-10}M$) concentrations of mercury or its compounds. Among these one could mention polarographic methods, particularly electrochemical stripping voltammetry.

Both mercurous and mercuric ions give rise to well-defined reversible reduction waves on mercury electrodes, in acid as well as in alkaline media, in the presence of a large number of complexing agents /296, 297/. Reduction waves corresponding to mercury ions can be, therefore, used for determining mercury and its compounds, especially organomercuric compounds, by polarographic means on mercury electrodes. The most sensitive polarographic methods for mercury compounds (particularly organomercuric compounds) have now reached a maximum sensitivity of $1 \times 10^{-7}M$ /298-304/.

The sensitivity of polarographic methods can, however, be greatly improved (down to $1 \times 10^{-10}M$ Hg) by resorting to electrochemical stripping methods, which involve the initial formation of an amalgam or of a deposit of the species to be determined. Obviously, conventional stripping voltammetry, which involves a stationary mercury electrode, cannot be used for determining mercury and the working electrode must be a solid electrode. It appears that platinum electrodes are not appropriate to the intricate effects which occur on amalgamation of the electrode surface, which interfere in the determination and, additionally because mercury deposition depends on the state of the electrode surface /297/. If platinum electrodes are nevertheless used, pre-electrolysis at constant current seems to be more adequate than pre-electrolysis at constant potential. The redissolution process should be monitored by oscillopolarographic means.

The best results for microamounts of mercury by anodic stripping voltammetry were obtained with carbon electrodes, carrying out the pre-electrolysis at potentials between 0 and -1.0 V *vs.* SCE and using complexing media (alkali thiocyanates, halogenides, hydrochloric acid, ammonia, hydroxylamine) as supporting electrolytes /297/. The first attempts at determining mercury by stripping voltammetry with carbon electrodes showed that 0.2 ppm Hg can be determined in KNO_3 solution at pH 2 with a graphite electrode soaked in paraffin wax /297/.

One of the most interesting studies in this direction was carried out by Perone and Kretlow /305/, who investigated the possibility of determining mercury by stripping voltammetry in the 1 x 10^{-4} - 1 x 10^{-9}*M* concentration range by using a paraffin wax-soaked electrode in thiocyanate medium. Others /306-308/ also dealt with the carbon-electrode stripping voltammetry of mercury, considering problems such as the selection of the supporting electrolyte, influence of pH, sensitivity limit and application of the method in various media. Roizenblat and Veretina /309,310/ investigated some particular aspects of mercury behaviour during its determination by anodic stripping voltammetry and also the possibility of increasing the sensitivity of the determination by using the so-called "support effect." In the presence of cadmium, the lowest concentration determined was 3 x 10^{-9}*M*.

Another kind of carbon electrode used successfully for determining mercury by anodic stripping voltammetry is the vitreous carbon electrode shaped as a rod, a stationary disk, a rotatory disk or a rotatory ring-disk. Luong and Vydra /311/ used a vitreous carbon rotatory-disk electrode to investigate the sensitivity and selectivity of mercury determination by anodic stripping voltammetry. The pre-electrolysis step was carried out both at constant current and at constant potential. The former procedure gave better results when the current was maintained at 300 μA. Constant-potential pre-electrolysis turned out to be more selective, but the optimum experimental conditions had to be set up for each particular case and for each supporting electrolyte used. In non-complexing media, the anodic dissolution current reached a maximum after the Hg^{2+} ions had been deposited at potentials ranging from -0.75 to -1.00 V. In potassium thiocyanate complexing medium, the pre-electrolysis potential was set in the range -1.00 to -1.50 V *vs.* SCE; KSCN was finally recommended as supporting electrolyte for determining mercury with vitreous carbon electrodes. The optimum pH value was set at about 2; above pH 6, no anodic dissolution peaks were observed. In this way, mercury was determined in the 1 x 10^{-6}– 5 x 10^{-8}*M* range, analysis being also possible in the presence of ten times higher concentrations of Cu, Pb, Zn, Co and Cd in KSCN or $NaClO_4$ at pH 2. A vitreous carbon electrode was also proposed for determining mercury using 0.2*M* KSCN as supporting electrolyte, at pH 4, setting the pre-electrolysis potential at

-1.10 V and scanning linearly from -0.60 or -0.50 V *vs.* SCE /297/. Under these conditions, a maximum with E_p = O V *vs.* SCE was recorded, whose height depended linearly on mercury concentration in the 1 x 10^{-5} - 5 x 10^{-8}*M* range. This method was applied to determine mercury in waste waters; at concentrations usually found in such waters, Cu, Zn and Pb did not interfere. The selectivity could be improved by carrying out an electrolysis at -0.35 V *vs.* SCE after pre-elctrolysis and before the mercury anodic dissolution stage; this operation removed Cd, Se and As.

The vitreous carbon electrode was also successfully used by other workers to determine mercury in various media /312-318/. Similar good results were obtained by using a carbon paste working electrode /319/.

Although several papers have dealt with mercury determination by anodic stripping voltammetry with carbon electrodes (soaked graphite, carbon paste, vitreous carbon), the problem of the anodic electrodissolution of mercury from these electrode has been only sparingly investigated. Among the early attempts to do this, we could cite the work of Penev *et al.* /320/. They studied vitreous carbon and paraffin-soaked graphite electrodes, as well as the electrodissolution of the mercury microdeposits formed on them in various supporting electrolytes ($NaNO_3$, KCl, KSCN, HNO_3, H_2SO_4, HCl). The authors pointed out that no qualitative difference exists between the behaviour of mercury during electrodissolution from the soaked graphite electrode and from the vitreous carbon electrode. For concentrations lower than 1 x 10^{-7}*M*, a single current maximum appeared on the anodic electrodissolution curve. Energetically, this anodic maximum is characteristic of the electrodissolution of mercury bound to the carbon electrode surface. When the pre-electrolysis potential was shifted to more cathodic values, the current increased, passed through a maximum at about 0.900 V and then decreased slowly. In some supporting electrolytes (HNO_3, HCl, H_2SO_4), no maxima could be recorded on the anodic dissolution curves of mercury for concentrations lower than 7 x 10^{-6}*M*. Most likely, at pH $<$ 1 the fraction of the current which is caused by the discharge of the H^+ ions is large, since hydrogen occupies active centers on the electrode surface and thus prevents mercury deposition. At pH values higher than 2, the anodic dissolution curves comprised several peaks at potentials largers than 0.50 V *vs.* SCE.

During recent years, several studies have used the rotating ring-disk-electrode to get a better understanding of the process of the reduction of Hg^{2+} on solid electrodes /321-327/, but mainly to study the kinetics ofmercury electrodissolution from solid electrodes /328, 329/. Thus, Kiekens *et al.* 328, 329/ ascertained the valence of the mercury ions formed during mercury electrodissolution from a solid electrode. A survey of the literature data related to mercury electrodissolution from carbon shows that Hg^{2+} ions are preferentially formed in complexing electrolytes, whereas Hg_2^{2+} ions are formed in non-complexing electrolytes. We might however note an exception: according to Combert and Dozol /330/, electrodissolution of mercury from a vitreous carbon electrode, in nitric acid and perchloric acid, produces only Hg^{2+} ions.

The results of the experiments of Kiekens and co-workers suggested that, following the mercury electrodissolution, a chemical reaction takes place. It was assumed that the first Hg^{2+} ions formed react with the unoxidized mercury atoms which are still present on the electrode surface, leading to Hg_2^{2+} ion formation. This mechanism proposed for the anodic dissolution of mercury explains why the maxima obtained during electrodissolution in media with complexing action are about two times higher than those obtained during electrodissolution in non-complexing media, where almost half of the mercury deposit formed on the electrode can be stripped away from its surface by non-electrochemical means owing to the above mentioned disproportionation reaction. The complexing properties of the supporting electrolyte on the Hg^{2+} ion are very important during the mercury electrodissolution process.

Another type of solid electrode used successfully during recent years for determining mercury by anodic stripping voltammetry has been the gold electrode. In its various forms (stationary disk, rotating disk or ring-disk), this electrode was mainly used for determining mercury in sea water and waste waters /331-337/, in river water /338/ air /339/, fish /340/, wine 341,342/ or biological materials /343,344/. By anodic stripping voltammetry in its differential-pulse variant, a detection limit of $1 \times 10^{-10} M$ was reported in such cases.

For concentrations lower than $5 \times 10^{-7} M$, mercury determination by chrono-potentiometric stripping has become possible by using a vitreous carbon electrode /345/. Jagner and Aren /346-350/ and Rubel

and Lugowska /351/ determined mercury by potentiometric stripping in the 5-1000 ppb concentration range. The indirect determination of mercury is also possible by using the decrease of the dissolution maximum of mercury in iodide media; by this method, less than 1 x $10^{-7}M$ could be determined, but the calibration curve was not linear. Methylmercury was also determined, with a 2 x $10^{-8}M$ detection limit, by differential pulse stripping voltammetry with a layered-gold electrode /352/.

Neutron activation analysis

Although neutron activation analysis usually provides accurate results, it is rather expensive and frequently the results take long times. The fundamentals of the method, with special reference to organomercuric compounds, have been described by Pillay *et al.* /353/.

Determinations by this method require special conditions, e.g., compact samples, protected against moisture. To compact the samples, activated charcoal or graphite shaped as an electrode, on which the mercury contained in the sample was deposited under controlled conditons, has been used. Alexandrov /354/ concentrated mercury compounds contained in sea water on a PbS column, on which the retention was very good (above 98%). Similarly, lead diethyldithiocarbamate was used /355/, as well as some organic supports such as an oil of definite composition /356/ or a sulphurated aniline /357/. After preconcentration, the samples were irradiated with a flux of 1 x 10^{12} neutrons cm $^{-2}$ s^{-1}. Measurements were made either by a Ge(Li) detector /356/ or a spectrometric method /354/. The most used reactions so far have been $^{196}Hg(n,\gamma)$ ^{196}Hg and $^{202}Hg(n,\gamma)^{203}$ Hg. The former is not subject to interferences and allows the determination of about 2 ppm of mercury /358/. The latter introduces interferences with the $^{206}Pb(n,\beta)^{203}$ Hg or $^{203}Th(n,p)$-^{203}Hg reaction and hence is less used than the former. Neutron activation allows mercury to be determined in various biological samples /358-360/.

Flow injection analysis (f.i.a.)

Flow injection analysis, coupled with suitable detection methods, was used in some cases for mercury determinations. Marita *et al.* 361/

used f.i.a. by coupling it with a fluorescence reaction. A solution of the sample was injected in 0.1*M* HCl and the mixture was flowed with a 2% $SnCl_2$ solution; mercury was then separated and the extinction read at 184.9 and 253.7 nm. This method permitted about 35 analyses per hour to be carried out, with a variation coefficient less than 1% for the 1-20 ppb range.

Fluorescence quenching of rhodamine B by Hg(II) was advanced as a variant /362/; the percent content of mercury ranged from 91.5 and 105.7%. A f.i.a. system was also coupled with a c.v.a.a. spectrometer /144/.

Bearing in mind the increasing necessity of determining mercury continuously, it is very likely that f.i.a. will be further developed in the future.

Amalgmation techniques

Starting from the observation of Anderson *et al.* 363,364/ that mercury can be collected on a gold foil and then determined by a.a.s., a working technique was developed which has drawn the attention of many authors. This technique eliminates the difficulties originating from the different rates of vapourization or from the different repartitions of mercury between liquid and vapor phases, used in other methods. Since mercury collected on a suitable foil can be released rapidly into the absorption cell by simply heating the collector, the sensitivity is increased. The detection limit of this method is of about 0.1 ppm /365/. Mercury collection could be carried out on gold foil /113,125,154,204,366-375/, silver /369-373,376/377/, gold-coated platinum /378/, MnO_2 /379,380/, and metallic antimony /381/. Luca *et al.* 88,91/ used goal-soaked quartz wool in a similar working procedure.

Amalgamation techniques can be used to collect mercury from various media; the amalgamation step is usually followed by analysis in most cases by a.a.s.

Other methods of determining mercury

Sensors based on the variation of the vibration frequency of a gold-coated piezoelectric crystal were used to determine mercury in air

/382-384/ and in liquid samples /385/. The sensitivity of these methods is around 10^{-11} g. Some detectors based on variations of the resistance of a gold film permitted about 10^{-10} g of mercury in air to be determined /386,387/; such detectors were also adapted for the determination of mercury in liquid samples /368/.

Photoacoustic detectors were also applied to determine mercury /388/, the detection limit reaching 10^{-10} g. This method becomes very selective by first separating and preconcentrating mercury.

Enzymatic sensors, though having good sensitivity, have been little used so far to determine mercury /389/.

CONCLUSIONS

During recent years, the increasing interest in determining the mercury content of various samples, particularly in environmental samples, has led to the development of a large number of analytical methods. Most of these methods use atomic absorption and atomic fluorescence and permit the determination of mercury with good selectivity and sensitivity in a variety of samples. A wet or dry pre-treatment of the samples is, however, frequently required. Continuous or automated methods using this principle have also been proposed, allowing separate determination of the inorganic and organic compounds of mercury.

Chromatographic methods have the great advantage of permitting all the species in which mercury can be found to be determined. The literature reports a large number of analytical methods based either on gas chromatography or liquid chromatography.

Among electrochemical methods, the polarographic ones and particularly those based on electrochemical stripping proved to have a high sensitivity. Under certain conditions, these methods permit a differential determination of the organomercuric compounds and are comparable in sensitivity with atomic absorption analysis.

Although colorimetric methods for determining mercury have a sensitivity which is adequate to analyze a wide variety of samples, and are economic and accurate, they have been less and less used during the last years, mainly because of the numerous interferences which occur and because the results are affected by a large number of factors.

Neutron activation analysis has a good sensitivity and is the only non-destructive method; its wide-spread use is nevertheless hindered by the rather expensive instrumentation required.

A great interest has been aroused in the method based on the variation of the resistance of a gold film with the amount of absorbed mercury. Several instruments based on this principle have become available.

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