ISOTOPCENTRALEN/ATV

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ORIENTERENDE UNDERSØGELSE AF KVIKSØLVINDHOLD I GRUNDVAND NÆR BANEGRAVSDEPOT VED GRINDSTED

NOVEMBER 1984

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PPM/BL 348.70
1984-11-16

Til Ribe Amt

ORIENTERENDE UNDERSØGELSE AF KVIKSØLVINDHOLD I GRUNDVAND NÆR BANEGRAVSDEPOT VED GRINDSTED

København, d. 16. nov. 1984
for ISOTOPCENTRALEN

Poul Pheiffer Madsen

1. BAGGRUND OG FORMÅL

Nærværende undersøgelse er udført af Isotopcentralen (IC) på foranledning af Ribe Amtsråds tekniske forvaltning, jvf. overenskomst af 13. september 1984. Formålet med undersøgelsen har været at forbedre beslutningsgrundlaget for en evt. iværksættelse af større undersøgelser til belysning af risikoen for spredning af kviksølv i grundvandet omkring banegravsdepotet i Grindsted.

En mere detaljeret beskrivelse af baggrund og formål er givet i IC's undersøgelsesoplæg af 22. august 1984, (se bilag 1), hvor også undersøgelsesplan er angivet.

2. PRØVETAGNING

Den 9. oktober 1984 blev der med Teknisk Forvaltnings HCV-prøvetager (peristaltisk) udtaget ca. 1 l vand fra boringerne GLP 7 og GLP 8, jvf. kortet bilag 2.

Prøverne blev udtaget 1,5-2 m under terræn, efter at boringerne dagen før var blevet renpumpede.

Prøverne, der begge var af grålighvidt mælket udseende, transporteredes samme dag til IC's laboratorium i København. Filtrering blev foretaget gennem 0,45 µm membranfilter m.h.p. analyse af både suspenderet materiale og filtrat. Samme dag udtoges i kvartsampul en prøve af vandet i Trane Sø (Tronsø, jvf. kortet bilag 2) til bestemmelse af totalkviksølvindhold. Prøven blev ikke filtreret. Samtidig udtoges fra båd og med kajak-bundhenter en 26 cm lang kerne af sedimentet i søen. Ved gentagne forsøgsvise prøvetagninger fordelt over hele søen (dybder 1-2 m) registreredes en rimelig ensartet sedimenttype overalt.

Overfladesedimentet (0-ca. 5 cm) bestod af gråsort flokkuleret materiale, medens sedimentet i større dybder måtte karakteriseres som brunfarvet og tørveagtig, med varierende finhed af tørvedelen.

../2

Sedimentkernen transporteredes i lighed med vandprøverne til IC samme dag. Lagene 0-3 cm og 24-26 cm blev udprepareret til analyse.

3. ANALYSE

3.1 VANDPRØVER FRA BORINGER

Totalkviksølvbestemmelse i både filtrerede vandprøver og i frafiltreret partikulært materiale blev efter destruktion med kongevand foretaget ved flammeløs atomabsorptionsspektrometri (detektionsgrænse ned til 20 ng/l, med præcision bedre end 10%).

De filtrerede vandprøver blev desuden analyseret for indhold af totalt organisk kviksølv ved metode beskrevet i bilag 3.

3.2 VANDPRØVE FRA TRANE SØ (IKKE FILTRERET)

Totalkviksølvbestemmelse blev foretaget ved neutronaktiveringsanalyse, som beskrevet i bilag 4.

3.3 SEDIMENT FRA TRANE SØ

Totalkviksølvbestemmelse blev foretaget ved samme metode som for det partikulære materiale i vand fra boringer.

4. RESULTATER

4.1 VANDPRØVER FRA BORINGER

Boring	pH	Kviksølv µg/l opløst		Kviksølv µg/l partikulært (> 0,45 µm)	
		organisk	total	total	
GLP 7	7,25	< 0,06	1,5	2,0	3,5
GLP 8	7,80	< 0,06	0,8	1,7	2,5

../3

4.2 VANDPRØVE FRA TRANE SØ

Totalkviksølvindhold: 0,036 µg/l
pH : 4,4

4.3 SEDIMENT FRA TRANE SØ

Dybde cm	Tørstof %	total kviksølv ng/g tørstof
0-3	7,5	145
24-26	9,2	20

5. KOMMENTARER

5.1 BORINGER GLP 7 OG GLP 8

Indholdet af opløst kviksølv er mellem 1 og 2 størrelsesordener højere end forventeligt i uforurenet grundvand og spredningen af kviksølv fra banegravsdepotet er derfor evident. Mere end 90% af det opløste kviksølv foreligger på uorganisk form, dvs. den mindst akut giftige form.

Det høje indhold af partikulært kviksølv indikerer, at transport af kviksølvholdige partikler eller udfældning af transporteret opløst kviksølv har fundet sted.

5.2 TRANE SØ

Totalkviksølvkoncentrationen i vandfasen afviger ikke fra almindeligt forekommende koncentrationer i søvand.

Sedimentkoncentrationen viser ikke tegn på indstrømning af kviksølv med grundvandet. Koncentrationsforøgelsen i øverste sedimentlag i forhold til nederste lag er ca. 7 x, hvilket kan tilskrives udviklingen i atmosfærisk deposition af kviksølv.

../4

Sammenfattende for søen kan det derfor anføres, at der ikke er fundet tegn på, at transport fra banegravsdepotet til søen har fundet sted.

Projektbeskrivelse:

ORIENTERENDE UNDERSØGELSE AF KVIKSØLVINDHOLD I GRUNDVAND NÆR BANEGRAVSDEPOT VED GRINDSTED.

BAGGRUND OG FORMÅL

I Ribe Amtskommunes "Affaldsplanlægning, Plan 1984 - 1987" (maj 1984), fremgår det af bilag 1 A og 2,

- at kviksølv i banegravsdepotet er deponeret som tungtopløseligt mercurisulfid (HgS, ca. 7,5 tons) i perioden 1957 - 1962.

- at grundvandsstrømmen overvejende er fra NØ mod SV, d.v.s at den nærliggende Trane Sø er beliggende nedstrøms for depotet. Iflg. supplerende oplysninger modtaget fra Teknisk forvaltning er der tidligere målt mindre end 0,15 µg Hg/l i søen. Dette udelukker imidlertid ikke at søen kan være påvirket, idet søvand typisk vil indeholde 0,010 - 0,030 µg Hg/l.

- at der i to grundvandsboringer syd og sydvest for depotet er fundet grundvandskoncentrationer på 0,8 - 2 µg Hg/l. Da kviksølvindholdet i grundvand normalt vil kunne forventes at være 0,010 - 0,060 µg Hg/l, må en vis mobilitet af kviksølvet anses for at være konstateret.

På denne baggrund foreslår Isotopcentralen efter aftale med Teknisk forvaltning, at der foretages supplerende, orienterende analyser af vand og sediment i Trane Sø og af grundvand fra to boringer.

../2

Formålet med udførelsen af disse analyser er at forbedre beslutningsgrundlaget før en evt. iværksættelse af større undersøgelser til belysning af risikoen for spredning af kviksølv i grundvandet.

ANALYSER

1. Vand fra 2 stk. boringer nedstrøms depotet analyseres for kviksølv, idet tilstandsformen for dette bestemmes. Der bestemmes partikulært og opløst kviksølv. Det opløste kviksølv differentieres endvidere i organisk og uorganisk kviksølv. Resultaterne af disse analyser vil give værdifulde oplysninger, idet tilstandsformen er bestemmende for kviksølvets giftighed, opløselighed i grundvandet og tilbageholdelse i jordlagene.

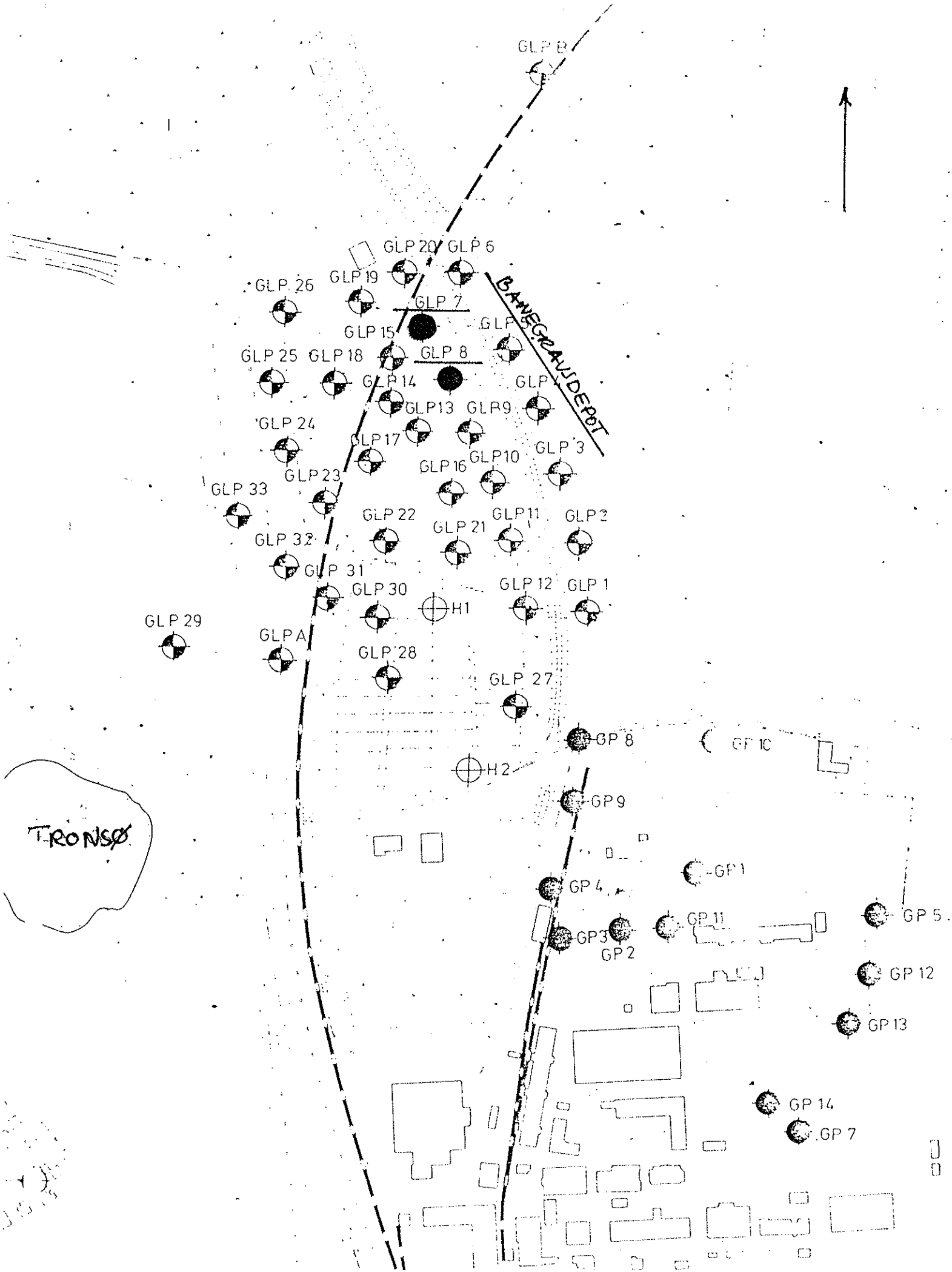
2 a. Vandet i Trane Sø analyseres for totalt opløst kviksølv med tilstrækkelig lav detektionsgrænse, d.v.s. ca. 0,001 µg Hg/l, hvorved det med sikkerhed kan afgøres, om niveauet er unormalt.

Fra søens sediment optages endvidere en kerne og der analyseres for kviksølv i to prøver fra henholdsvis top og bund i kernen.

2 b. Såfremt tilstrækkelig markant forskel i kviksølvindhold mellem top og bund kan konstateres, søges kernen dateret v.h.a. Pb-210 metoden, og yderligere prøver i kernen analyseres for kviksølv. Det vil derved være muligt at afgøre, om søen har fået væsentlige kviksølvmængder tilført via indtrængende grundvand og i givet fald, hvornår påvirkningen er påbegyndt.

Dette punkt iværksættes først efter aftale med amtets tekniske forvaltning.

../3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GLP 23
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GLP 22
GLP 21
GLP11
GLP 32
GLP 31
GLP 30
GLP 12
GLP 1
H1
GLP 29
GLP A
GLP 28
GLP 27
BANEGRAVJDEPOT
GP 8
GP 10
H2
GP 9
TRONSØ
GP 1
GP 4
GP 11
GP 5
GP3
GP 2
GP 12
GP 13
GP 14
GP 7

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Comparison of Different Analytical Techniques for the Determination of Organic Mercury

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Methods for the determination of (1) total organic mercury (Hg) using an extraction + neutron activation analysis, (2) the sum of methyl-Hg + phenyl-Hg using $^{131}I^-$-Cl^- exchange and (3) methyl-Hg using two different Westöö modifications, have been compared. Sample materials were 8 falcon livers, 5 pike livers and 2 pike muscles. Although differences were found between the methods, interaction effects caused by either sample inhomogeneity or bad performance of the analytical methods impeded a clear interpretation of the comparison. Total Hg in the samples was determined by neutron activation analysis (NAA) and atomic absorption spectrometry. The accuracy of the total Hg determination using NAA was verified by the analysis of certified reference material.

In addition to the other organic Hg determinations phenyl-Hg was determined separately in some of the samples by an isotope exchange method using $^{203}Hg^{2+}$.

The main conclusion of the study was that there is a demand for reference materials certified for at least total organic Hg and methyl-Hg.

INTRODUCTION

The toxicity of alkylmercuries have been known for decades.[1,2] This knowledge, added to an understanding of the ecological transformation of mercury (Hg) into potentially more hazardous compounds, has motivated increased concern about Hg levels in the environment. Methods for the detection of small amounts of Hg, but

also to identify the compounds containing it are therefore of considerable importance.

Several studies have shown that a large fraction of the Hg assimilated into plant and animal tissues is present as the toxic methyl-Hg (see e.g., Ref. 3). The most widely employed technique for the determination of methyl-Hg in biological material is still based upon the procedure devised by Gage[4] in 1961 and later developed into a gas chromatographic (GC) method by Westöö.[5,6] The need, however, for greater specificity regarding other organomercury compounds and simple and more sensitive methods has led to the development of a variety of different procedures, e.g., the combination of Westöö's GC procedure with atomic absorption spectrometry (AAS)[7] and the combination of the Westöö procedure, without the GC, with AAS[8] or neutron activation analysis (NAA).[9] The latter two combinations are used for the determination of total organic mercury. Other sensitive techniques employ thin-layer chromatography of dithizone extracts combined with AAS,[10] and GC after separation of methyl-Hg with the aid of hydrocyanic acid and cysteine paper.[11] Greater sensitivity together with higher specificity are achieved using GC combined with microwave emission spectrometry[12] or mass spectrometry,[13] and more recently by liquid chromatography with differential-pulse electrochemical detection.[14] Another group of common methods are the selective reduction methods using either $SnCl_2/NaBH_4$ (Ref. 15) or $SnCl_2/CdCl_2$ (Ref. 16), while the use of radioisotope methods like exchange reactions with either $^{203}Hg^{2+}$ (Ref. 17) or $^{131}I^-$ (Ref. 18) seem less abundant.

Contrary to this diversity of methods the occurrence of certified reference materials is very limited. On that basis it seems difficult to evaluate the performance of all these methods unless direct comparisons are made.

Aiming to check our analytical techniques for the determination of organic mercury we therefore compared our methods with methods used on a routine basis by other laboratories. The results of these collaborative tests are reported in this work.

EXPERIMENTAL

The methods used, together with their primary references, are listed

TABLE I

Methods used for the determination of organic mercury.

Method No.	Analyte	Principle	Reference	Remark
1	total Hg	NAA[a]	19	DIC[c]
2	total Hg	AAS[b]	24	
3	total organic Hg	extraction + NAA	9	DIC
4	Σ (methyl-Hg + phenyl-Hg)	$^{131}I^-$-Cl^- exchange	20	DIC
5	methyl-Hg	Westöö modification	22	
6	methyl-Hg	Westöö modification	23	
7	phenyl-Hg	$^{203}Hg^{2+}$-Hg^{2+} exchange	21	DIC

[a]NAA, neutron activation analysis.
[b]AAS, atomic absorption spectrometry.
[c]DIC, Danish Isotope Centre.

in Table I. The methods employed by the Danish Isotope Centre (DIC) were methods No. 1, 3, 4 and 7 shortly described below.

Total Hg was determined by *Method No. 1* using radiochemical NAA.

In *Method No. 3* total organic Hg was determined using a modified Westöö extraction, i.e., extraction of the organic Hg with toluene and back-extraction with a cysteine acetate solution, followed by NAA of the cysteine acetate solution.

Method No. 4 was employed for the determination of the sum of methyl-Hg and phenyl-Hg using the exchange reaction between their chlorides and the radioactive $^{131}I^-$. The exchange reaction, which is a two-phase reaction, employs as its first part a separation of the methyl-Hg and phenyl-Hg from the sample using several extraction and purification steps ending up with a toluene phase (cf. Ref 18). To the toluene phase is added $^{131}I^-$ in an aqueous ascorbic acid solution causing an exchange between the chloride of methyl-Hg-Cl and phenyl-Hg-Cl in the toluene phase and $^{131}I^-$ in the water phase. The exchange reaction has been shown to be selective, fast and quantitative as long as $[Cl^-]/[I^-] \leqq 600$; after only 1 min the measured activity in the toluene phase is proportional[18] to the concentration of the sum of methyl-Hg and phenyl-Hg. The

concentration was determined by comparison with standards treated similar to the samples.

Method No. 7 was used for the determination of phenyl-Hg. It is based on the isotope exchange between the Hg of phenyl-Hg-Cl and the radioactive $^{203}Hg^{2+}$. The reaction is carried out by addition of HCl and $^{203}HgCl_4^{2-}$ to the sample, followed by 20 min of standing (exchange reaction going on), isolation of the phenyl-^{203}Hg/Hg-Cl by extraction with toluene and radioactivity measurement of the toluene. As long as inorganic Hg is added in excess the exchange reaction will cause no significant fall in the specific activity of the ^{203}Hg and the activity of the toluene phase will be proportional to the phenyl-Hg concentration. The method has been shown to be very selective also towards methyl-Hg (cf. Ref. 21). The concentration was determined by comparison with similar treated standards.

Also included in Table I are the methods used by the other two laboratories, i.e., *Method No. 2*, total Hg determination using AAS and *Methods No. 5* and *6*, two Westöö sample modifications for methyl-Hg determination (extractions: sample→toluene→cystein acetate solution→benzene—GC with electron capture detection). The first modification used $CuSO_4$ in the first extraction step to displace sulphur-bound Hg.

Sample materials were falcon livers obtained from West Greenlandic falcons and pike liver and muscle samples from Wänern, Sweden. A total of 8 falcon livers, 5 pike livers and 2 pike muscles were analysed.

The samples were homogenized prior to analysis. Due to lack of sample material not all methods were employed on each sample. In each case determinations were carried out in duplicate.

RESULTS AND DISCUSSION

The accuracy of the total Hg determination using *Method No. 1* is documented by the results of analyses of various reference materials certified by the National Bureau of Standards in U.S.A. as shown in Table II.

The relative precision of the methods used by us was generally better than 10%.

TABLE II
Analysis results for NBS[a] standard reference materials using neutron activation analysis.[b]

	Our result ± S.E.[c] (ng/g dry matter)		Certified by NBS (ng/g dry matter)
NBS 1571 Orchard leaves	151 ± 7	(22)	155 ± 15
NBS 1645 River sediment	949 ± 55	(10)	1100 ± 500
NBS 1577 Bovine liver	16.2 ± 0.8	(6)	16 ± 2
NBS 1566 Oyster tissue	49 ± 7	(4)	57 ± 15
NBS 1632a Coal	129 ± 10	(8)	130 ± 30

[a]NBS, National Bureau of Standards (U.S.A.).
[b]Ref. 19.
[c]Numbers in parentheses indicate number of determinations.

Falcons

The results for the falcon livers are shown in Table III. The AAS determination of total Hg tended to give a higher result than the NAA determination at the lower concentrations. No statistical difference, however, could be found between the methods when the logarithmized data were tested by a paired Student *t*-test.

The phenyl-Hg constituted only on one occasion a significant amount of the total Hg content in the falcon livers. The sum of methyl-Hg and phenyl-Hg, determined by the $^{131}I^-$-Cl^--exchange, *Method No. 4*, therefore reflects the methyl-Hg concentration. If we make the reasonable assumption that the total organic Hg is mainly methyl-Hg (cf. Ref. 3) the results within the broken line rectangle in Table III show the methyl-Hg content in these specific samples measured by four different methods, i.e., *Methods No. 3*, *4*, *5* and *6*. These results as percentage of the total Hg content measured by NAA, were subjected to a two-sided analysis of variance, using a mixed model with samples as random and methods as fixed factors (cf. Ref. 25).

The results of this analysis revealed a difference between the methods on a 10% significance level. The reason for the low significance was a highly significant interaction effect caused by

TABLE III

Results for falcon livers (mean ± S.E. of two separate determinations).[a]

Method No.	1	2	3	4	5	6	7
Analyte:	Total Hg	Total Hg	Total organic Hg	Σ (Methyl-Hg + phenyl-Hg)	Methyl-Hg	Methyl-Hg	Phenyl-Hg
Sample 1	0.217 ± 0.003 (100)	0.29 ± 0.01 (131)	0.204 ± 0.008 (94)				0.010 ± 0.001 (4.7)
Sample 2	0.602 ± 0.001 (100)	0.60 ± 0.04 (100)	0.574 ± 0.011 (95)			0.52 (86)	
Sample 3	1.05 ± 0.07 (100)	1.22 ± 0.04 (116)	0.90 ± 0.08 (86)			0.92 (88)	0.004 (0.04)
Sample 4	1.24 ± 0.04 (100)	1.26 ± 0.01 (102)	1.12 ± 0.10 (90)				0.004 (0.03)
Sample 5	1.52 ± 0.01 (100)	1.35 ± 0.15 (89)	1.24 ± 0.01 (89)	1.38 ± 0.27 (91)	1.02 ± 0.08 (67)	1.16 ± 0.14 (76)	0.0011 ± 0.0002 (0.007)
Sample 6	2.24 ± 0.04 (100)	2.29 ± 0.08 (102)	1.93 ± 0.05 (86)	1.58 ± 0.18 (71)	1.22 ± 0.23 (54)	1.72 ± 0.06 (77)	0.0005 ± 0.0002 (0.02)
Sample 7	2.59 ± 0.25 (100)	2.41 ± 0.08 (93)	1.87 ± 0.21 (72)	2.71 ± 0.27 (105)	1.07 ± 0.10 (41)	2.07 ± 0.17 (80)	
Sample 8	3.60 ± 0.07 (100)	3.50 ± 0.02 (97)	3.23 ± 0.02 (90)				0.0011 ± 0.0002 (0.03)

[a]Result as percentage of the result of method No. 1 shown in parentheses.

either bad performance of the methods or by sample inhomogeneity. The significance, however, was found to be caused by *Method No. 5*, which generally produced lower results on these samples than *Methods No. 3*, *4* and *6*.

Comparing *Methods No. 5* and *6* this finding was rather surprising and unexpected. Both methods are Westöö modifications, the only difference between them being the use of $CuSO_4$ in *Method No. 5* in order to mask any free sulfhydryl groups and displace Hg bound to sulphur.[26] Although this procedure has been proved to be inefficient compared to the use of proteolytic enzymes[27] one would still expect *Method No. 5* to produce results equal to or greater than results produced by *Method No. 6*.

Pikes

The results for the pike livers and muscles are shown in Table IV. Total Hg was determined by NAA (*Method No. 1*). Total organic Hg, the sum of methyl-Hg and phenyl-Hg, and methyl-Hg were determined by *Methods No. 3*, *4* and *5* (cf. Table I), respectively. Phenyl-Hg was not determined but is not likely to occur in significant amounts (cf. Ref. 14). For the pike livers only two results were obtained using *Method No. 4*. These results agree with the ones of *Method No. 5*.

The results within the broken-line rectangles in Table IV were subjected to the same two-sided analysis of variance as the results of the falcon livers. The results, however, are very sparse and the following findings should only be considered indicative.

For the pike livers neither the method factor nor the interaction was found to be significant, i.e., no difference was found between *Methods No. 3* and *5*.

For the pike muscles the interaction effect overshadowed any differences between the methods. Again this interaction effect might be caused by sample inhomogeneity or bad method performance. Comparing the results two by two, however, revealed the results of *Method No. 5* in all but one case to be significantly lower than the results of *Methods No. 3* and *4*.

A possible, but not very likely explanation of the differences, could be the presence of a significant amount of phenyl-Hg in the samples, which would be included in the results of *Methods No. 3* and *4*.

TABLE IV

Results for pike livers and muscles (mean ± S.E. of two separate determinations).[a]

Method No.:	1	3	4	5
Analyte :	Total Hg	Total organic Hg	Σ (Methyl-Hg + phenyl-Hg)	Methyl-Hg
Pike liver 1	0.351 ± 0.018 (100)	0.24 ± 0.06 (69)		0.27 ± 0.04 (77)
2	0.440 ± 0.005 (100)	0.16 ± 0.03 (37)		0.26 ± 0.06 (59)
3	0.177 ± 0.010 (100)		0.12 (68)	0.16 ± 0.01 (90)
4	0.481 ± 0.008 (100)	0.23 (48)		0.26 ± 0.04 (54)
5	0.279 ± 0.022 (100)		0.21 (75)	0.24 ± 0.03 (86)
Pike muscle 1	0.596 ± 0.0020 (100)	0.52 ± 0.04[b] (86)	0.66 ± 0.03[b] (111)	0.29 ± 0.04[c] (49)
2	0.686 ± 0.002 (100)	0.63 ± 0.04[b] (91)	0.43 ± 0.11 (63)	0.27 ± 0.04[c] (39)

[a]Results as percentage of the result of method No. 1 shown in parentheses.
[b,c]Difference between results marked a and b at a 5% significance level.

CONCLUSIONS

The purpose of this study was to evaluate the performance of the methods used by our laboratory for the determination of organic Hg by comparison with common and well established routine methods. The comparison with one of these methods showed good agreement, while some discrepancies were found regarding the comparison with the second routine method. As no other value than the total Hg content could be determined with a documented accuracy using certified standard reference materials none of the results could, however, be rejected as being wrong. Dissimilarities might be attributed to sample inhomogeneity or bad performance of any of the methods. On this basis the main conclusion of this work must be

that there is a great need for the development of reference materials certified for at least total organic Hg and methyl-Hg.

Acknowledgement

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LOW LEVEL MERCURY ANALYSIS BY NEUTRON ACTIVATION ANALYSIS

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During the years 1974–77 about 200 low level mercury analyses on samples with less than 1000 ng Hg/kg were made at the Danish Isotope Centre. This paper describes our method of neutron activation analysis for low level mercury analysis. The accuracy of the mercury analyses is shown by the results of the determinations on NBS standard, SRM 1642, and on intercalibration analyses. The accuracy found is better than 10% for samples with about 100–300 ng Hg/kg and better than 10 ng Hg/kg for samples with less than 100 ng Hg/kg. The limit of detection for the analyses is about 1–5 ng Hg/kg, depending on the sample and the exact method of analysis. The lowest standard deviations on duplicate analyses are about 1 ng Hg/kg. The general level found in sea water is about 10 ng Hg/kg, in ground water about 50 ng Hg/kg, and in rain water about 100 ng Hg/kg.

Introduction

The problems of mercury in the environment have been discussed considerably. From the analytical results the level of output from man-made sources has also been discussed.

For the low level samples (water, Greenland ice) the levels of mercury analysed by different laboratories show great discrepancies. In this paper the low level mercury analyses performed at the Danish Isotope Centre by neutron activation analysis according to SJÖSTRAND[1] are described.

Experimental

Collecting and preparation of the samples

3 or 10 ml quartz ampoules are rinsed in nitric acid or more recently by heating to about 500 °C in 2 hours. The samples are transferred into the quartz ampoules and sealed with the sample part cooled in an ice water mixture. Blanks are empty ampoules, scaled at the same time and place as the samples. Different low level samples are prepared in the following way:

Greenland ice samples are prepared by rinsing the ice core by melting or cutting. Afterwards a smaller sample is taken by further melting or cutting, promptly

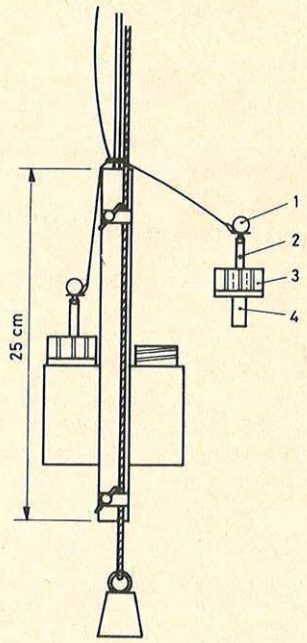

Fig. 1. Sample collector. 1 – Glass stopper; 2 – tygon tube; 3 – screw cap; 4 – evacuated ampoule (3 ml)

transferred to a 35 ml flask, and introduced into the quartz ampoule with a pipette and sealed immediately.

Some sea water samples are taken in a sample collector, transferred to 0.5–1 l bottles, and transferred to the quartz ampoules and sealed. Other sea water samples are taken directly in the evacuated quarts ampoules with the sample collector shown in Fig. 1, and the quartz ampoule is sealed immediately at place of sampling.

Ground water samples are collected in 0.5–1 l bottles with 10% concentrated nitric acid and sealed in the quartz ampoules usually one day after the samples are taken.

Rain water samples are collected via a 20 cm funnel and a nylon filter (1 mm holes) in 5 l polyethylene bottles with 100 ml conservation mixture. The conservation mixture contains 64 ml concentrated nitric acid, 2 μg gold as goldtetrachloride ion, and demineralised water to 100 ml. 1 to 2 litres are collected each month and sealed in quartz ampoules a few days after.

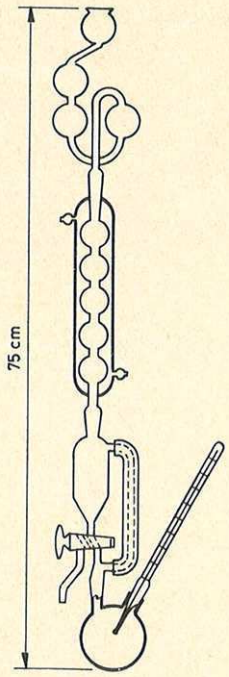

Fig. 2. Bethge distillation apparatus

Mercury analysis

The analysis for mercury is done according to SJÖSTRAND[1] with some modifications. The method is described briefly below:

The quartz ampoules with samples and standards are irradiated at a flux of $5 \cdot 10^{12}$ n · cm^{-2} · sec^{-1} in 48 hours at Kjeller (Norway). After irradiation each ampoule is rinsed with acetone, boiling aqua regia, water and alcohol. Then the ampoule is cooled in liquid nitrogen, placed in a 50 ml polyethylene flask with 20 mg inactive mercury carrier dissolved in 5 ml concentrated nitric acid. The ampoule is crushed in the closed polyethylene flask. The contents are mixed by shaking. The contents, except for pieces of quartz are transferred to a Bethge distillation apparatus (Fig. 2), and the polyethylene flask is again shaken with a 10 ml mixture of concentrated nitric and sulfuric acid, and this is also transferred to the Bethge apparatus. The contents are decomposed by heating. Afterwards perchloric acid and glycine is added and mercury is destilled off as mercury chloride.

The destillate is transfered to polyethylene beakers with gold and platinium foils as elektrodes, and the mercury is deposited on the gold by electrolysing for

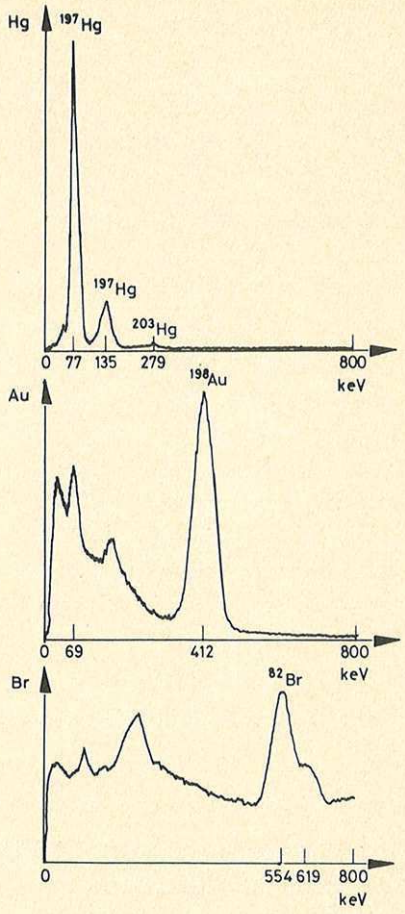

Fig. 3. Gamma spectres from neutron irradiated mercury, gold and bromine

about 17 hours, and the chemical yield is determined by weighing the gold foil. Standards containing 2 μg and 20 ng Hg are treated similarly, but without the digestion step. Standards are chemically separated in another laboratory to avoid contamination of the low level samples. The γ-irradiation from the ^{197}Hg deposited on the gold foil is measured in a NaI(Tl) well crystal, connected to a multi-channel analyser (Intertechnique). Energies from 0–800 keV are measured, see Fig. 3.

In the sea water samples there are heavy interferences from ^{82}Br when using the usual chemical separation, see Figs 3 and 4. In order to minimize these interferences a sulfide precipitation is executed in this way: After decomposing the

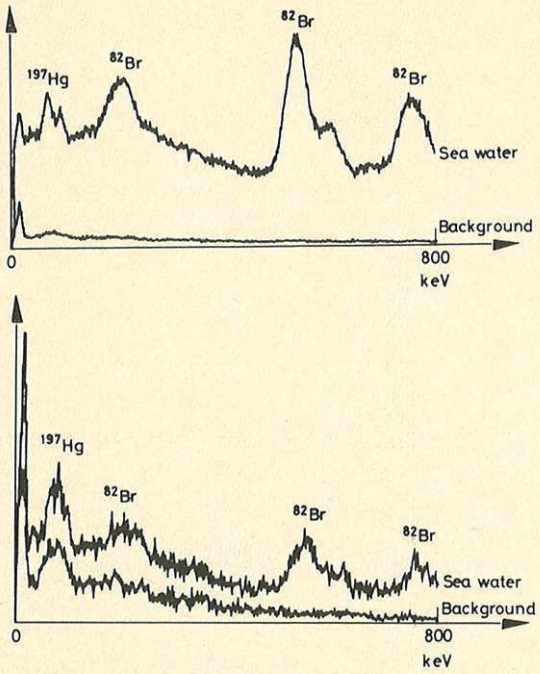

Fig. 4. Gamma spectres from neutron irradiated and chemically separated sea water

ımple, the solution is neutralised with ammonium hydroxide and the mercury is recipitated as sulfide with thioacetamide. The precipitation is filtered off and di-ɛsted again with a mixture of concentrated sulfuric and nitric acid.

In rain water samples there are heavy interferences from ^{198}Au because of the ıdded goldtetrachloride as conservation, see Figs 3 and 5. To avoid this, the ıercury deposited on the gold foil is dissolved in half concentrated nitric acid and ı extra electrolysis is undertaken.

What might be left of ^{82}Br and ^{198}Au is corrected for by experimentally found ıctors. The corrections are usually less than 10%.

The calculations are done according to the measured activities, the chemical ield, and the sample weight. The chemical yield is found by weighing the gold ɔil before and after the electrolysis.

The calculations of the mercury concentrations are done according to the for-ıular:

$$X = (\text{netto cpm}) \cdot \frac{1}{\text{yield}} \cdot \frac{Hg_{std}}{\text{std cpm}} \cdot \frac{1}{\text{weight}} \qquad (1)$$

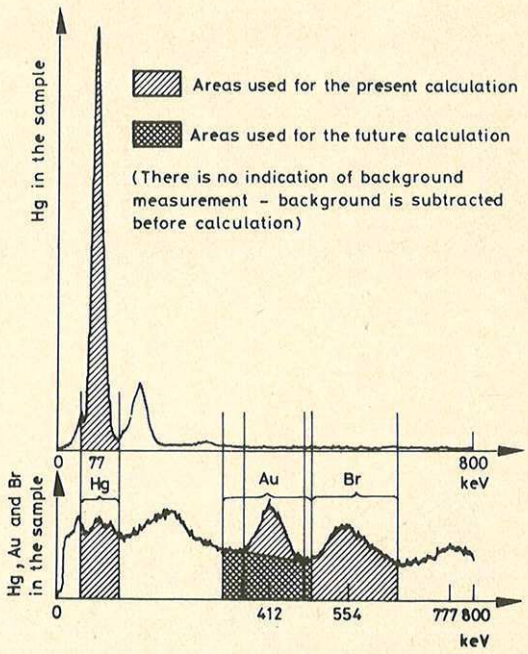

Fig. 5. Gamma spectres. Calculation of mercury concentration

where netto cpm – cpm, corrected for background;
yield – chemical yield;
Hg_{std} – weight of mercury in the standard;
std cpm – netto cpm for the standard, corrected for background;
weight – weight of the sample.

At present the netto cpm is calculated in different ways depending on the interferences from gold and bromine. With no interferences:

(a)
$$\text{netto cpm} = \frac{Hg}{T} - Hg_B \qquad (2)$$

where Hg – gross count for mercury in the measuring area for mercury (see Fig. 5);
Hg_B – background, cpm, in the same measuring area. Mean of two measurements made before and after the samples;
T – measuring time for the sample.

With interference from gold, present calculations:

b) $$\text{netto cpm} = \frac{Hg}{T} - Hg_B - \left(\frac{Au}{T} - Au_B\right) \cdot Au_F \qquad (3)$$

where Au – gross counts for gold in the measuring area for gold (see Fig. 5);
Au_B – background, cpm, in the same measuring area. Mean of two measurements;
Au_F – correction factor for gold in the mercury measuring area.

With interference from bromine, present calculations:

c) $$\text{netto cpm} = \frac{Hg}{T} - Hg_B - \left(\frac{Br}{T} - Br_B\right) \cdot Br_F \qquad (4)$$

where Br – gross counts for bromine in the measuring area for bromine (see Fig. 5);
Br_B – background, cpm in the same measuring area. Mean of two calculations;
Br_F – correction factor for bromine in the mercury measuring area.

With interference from both gold and bromine (background for gold is found by the trapez method, see Fig. 5):

d) $$\text{netto cpm} = \frac{Hg}{T} - Hg_B - \left(\frac{Au}{T} - \frac{A_1 + A_2}{2T}\right)Au_F - \left(\frac{Br}{T} - Br_B\right) \cdot Br_F \qquad (5)$$

where A_1 – counts in the first channel of the gold area;
A_2 – counts in the last channel of the gold area.

In the new method for calculation formular (a) is used when there is no interference.

When interference from gold and/or bromine is found the following formular is used:

e) $$\text{netto cpm} = \frac{Hg}{T} - Hg_B - \left(\frac{Au}{T} - Au_B\right) \cdot Au_F - \left(\frac{Br}{T} - Br_B\right) \cdot Br_F \qquad (6)$$

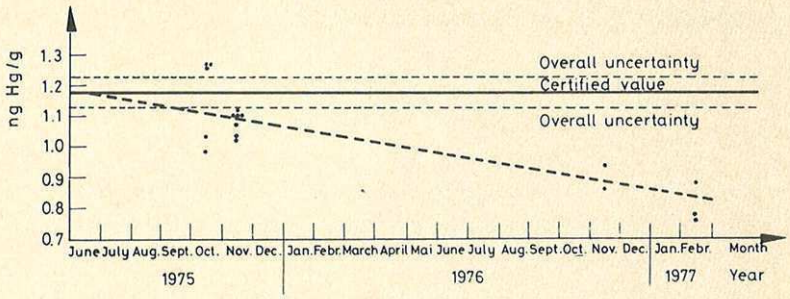

Fig. 6. Results for NBS-SRM 1642, purchased June 1975

So the measured background for the whole area is always used and in Br_F are Au_F are incalculated how much bromine will be in the gold area (about 70% of the bromine area) and how much gold will be in the bromine area (less than 1% of the gold area).

The standard deviations on counting statistics are calculated from standard deviations on the gross counts and the background counts from mercury, gold, and bromine areas, and on the correction factors on gold and bromine. Standard deviations on the chemical yield and the standards are insignificant for low level analysis.

Results

It is not possible to acquire standard material at the level of sea water, but we have analysed the NBS standard, SRM 1642 (mercury in water, trace) with a level of about 1000 ng Hg/kg. Results from different sealing dates are shown in Fig. 6. The results show that some losses appear with time. NBS states that this standard can be used one year after purchase. The solution is conserved with nitric acid and goldetrachchloride. Other standard materials analysed during the same period does not show this decrease in mercury concentration.

Attempts were made to dilute the NBS-SRM 1642 in order to certify the low level found in Greenland ice and sea water. Results are shown in Table 1. The expected order of magnitude is found for these results.

We have participated in an ICES intercalibration which has been reported by ÓLOFSSON[2,3] in April 1976. The arithmetical mean of sea water analyses from 5 laboratories with reasonable results was 6.6 ± 2 ng Hg/l. We found 31, 6 and 3 ng Hg/kg. Our first value must result from a contaminated sample, but the rest do agree well with the mean. We had at the same time and in about the same spot

Table 1
Results for NBS-SRM 1692 and dilution of this standard, analysed 1975 and 1977. Standard deviation is calculated from the replicate analyses

Year	Number of analyses	Results, ng Hg/kg	Calculated from analysis of SRM-1692 and dilution medium, ng Hg/kg
1975 SRM 1642	7	1077 ± 39	
Dilution medium (H_2O)	2	10 ± 2	
I. Dilution: 1 to 10	6	117 ± 11	127 ± 5
II. Dilution: 1 to 100	6	16 ± 2	22 ± 4
1977 SRM 1642	4	826 ± 33	
Dilution medium ($AuCl_4^- + HNO_3 + H_2O$)	4	51 ± 2	
I. Dilution: 1 to 10	6	114 ± 7	129 ± 2
II. Dilution: 1 to 100	5	87 ± 4	81 ± 2

samples collected in our own sample collector and we found results of 13 and 3 ng Hg/kg. In a spiked sample from the same intercalibration 10 laboratories with reasonable results found a mean of 137 ± 31 ng Hg/l and we found 131 and 121 ng Hg/kg.

In March 1977 we have participated in the Baltic Intercalibration Workshop.[4,5] The overall means of selected results of 6 sea water samples were 242 ± 50, 27 ± 9, 27 ± 9, 52 ± 10, 34 ± 21 and 37 ± 25 ng Hg/l, and our determinations were respectively 242/229, 21, 22, 43, 21, 21 ng Hg/kg. The interlaboratory standard deviation on each sample was 18–68%.

We have analysed sea water from the Sound and the results are published in the Danish Belt Project,[6] see Fig. 7.

Mercury in Greenland ice is often referred to and has been analysed by WEISS.[7] The Danish Isotope Centre has also analysed mercury in Greenland ice and we find a level which is one order of magnitude lower than the results found by WEISS.[8] We believe that WEISS's results show the contamination level rather than the true values. We have analysed the Greenland ice in different series during 1975 and 1976, and we got good agreement in duplicates within one series (which might be calculated with the same standards) and in different series (which surely are calculated with different standards). In Table 2 are shown the results for Greenland ice analysed in the different series.

Table 2
Mercury in Greenland ice

Ice core and snow-fall dating	Analyses, ng Hg/kg			
	1. series	2. series	3. series	4. series
C 1773	17	18		
C 1774	13	8		
C 1775	4	5		
C 1776	5/4			
C 1777	7±3	3		
C 1778	6±3	5		
C 1779	12±6	6		
C 1780	3	5		
C 1781	5	4		
C 1782	5	2		
C 1783				34
C 1785				3
C 1786				2/4
D 1902 Spring	6/5			
D 1902 Autumn	7±2			5±3
D 1905 Spring	7/4			
D 1905 Autumn	4			8±3
D 1927	8			
C 1913	4		15	
C 1926	6			7
C 1936	2/3			
C 1937	6		8	
C 1938	12			10
C 1957	11/12			
C 1960	12		12	
C 1964	16/10			
C 1969	11		12	
C 1970	7		10	
C 1971	9		13	

D – Ice core from Dye 3;
C – ice core from Crête.
Ice core and dating obtained from Geophysical Isotope Laboratory, University of Copenhagen. The standard deviation due to counting statistics is ≤ 1 unless otherwise written.

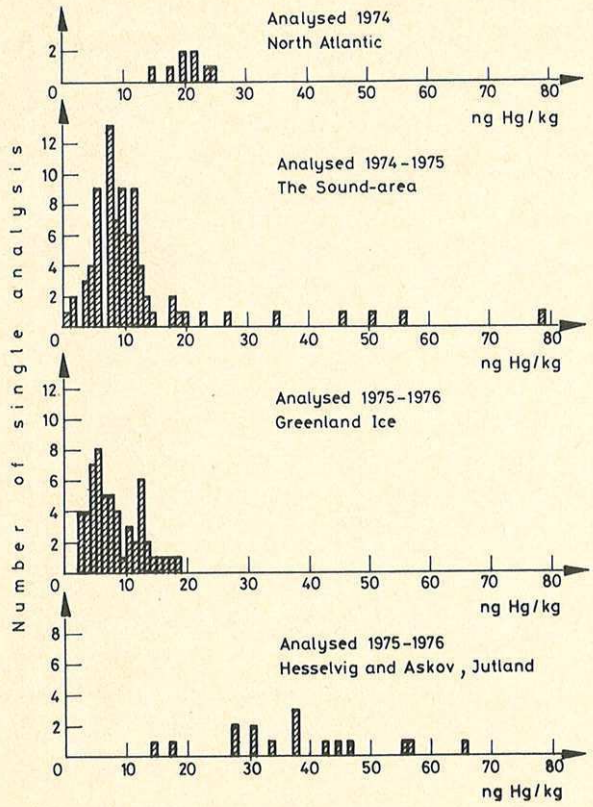

Fig. 7. Results for sea water, Greenland ice, and ground water

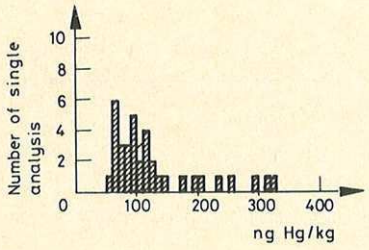

Fig. 8. Results for rainfall (precipitation)

Table 3 shows the standard deviations calculated from counting statistics, and duplicate analyses on sea water and Greenland ice. The results show good agreements above 1 ng Hg/kg in standard deviations on counting statistics.

Table 3
Low level mercury analyses. Standard deviations on single values

Sample	Number of duplicates	Standard deviation ng Hg/kg	
		Calculated, counting statistics	From duplicates
Sea water			
Sample collector from	7	2.3 (mean)	0.9
Danish Isotope Centre with particulate matter	3	2–3	20
From 0.5–1 l bottles	4	2–3	1.2
Greenland ice			
Same series	7	⩽1	1.4
Different series	14	⩽1	1.3
S.D. on counting statistics >1	5	4.8 (mean)	2.3

Figs 7 and 8 show the results on sea water, Greenland ice, ground water and precipitation.

The values of the blanks are usually about 0–3 ng Hg/kg for the low level samples. Only few analyses with low counting statistics on the blanks were made.

Discussion and conclusion

During the years 1974–77 about 200 low level mercury analyses were made at the Danish Isotope Centre.

The original procedure was modified for use in the low level analysis in order to increase sensitivity, eliminate interference, and diminish mercury loss and contamination risks, as explained below:

Sensitivity was increased by using larger volume of sample (3 or 10 ml ampoules versus 0.3 ml), and increasing the neutron dose by a factor of 5.

Interference from gold and bromine was corrected for by experimentally found factors.

Loss of mercury which might appear during crushing of the ampoule was avoided by cooling the rinsed ampoule in liquid nitrogen before breaking.

The risk of contamination of the sample in the laboratory was minimized by using new polyethylene beakers for each electrolysis and carrying out all operations on low level samples in an isolated, clean laboratory with separate glass-ware.

Future calculations will be done only on the measured background. The measured background for the whole area is more accurate than the background found by the trapez method, according to the counting statistics.

Analyses of the NBS-SRM 1642 and of the dilution of this standard demonstrated that the accuracy of the analyses was in the right order of magnitude.

In the ICES intercalibration on sea water three analyses out of four were 1 to 4 ng Hg/kg from the mean on 6.6 ± 2 ng Hg/l. For the spiked sea water sample the mean was 137 ± 31 ng Hg/l, and we found 6 and 16 ng Hg/kg lower than the mean.

Results from the Baltic Intercalibration Workshop showed 18–68% interlaboratory standard deviation on 6 sea water samples, where one was spiked. All results from the Danish Isotope Centre were within this standard deviation.

From the results on the intercalibration and the NBS standard it is not possible to give exact values of the accuracy of the method. For the results below 10 ng Hg/kg the analysed values are usually less than 10 ng Hg/kg from the expected or mean value. For the results at 100–300 ng Hg/kg analysed values are usually less than 10% from the expected or mean value. The accuracy is thus considered better than 10% for values above 100 ng Hg/kg and better than 10 ng Hg/kg for values below 100 ng Hg/kg.

When the standard deviation on the mercury concentration calculated from counting statistics is above 1, the standard deviation for duplicates is usually not higher. A practical limit for standard deviations from duplicate analyses is thus 1 ng Hg/kg. The levels of the blanks were usually 0–3 ng Hg/kg. More analyses on blanks with low standard deviation on counting statistics will show the influence from these blanks.

For the low level analyses the risks of contamination is great even when the samples are collected with great caution. It is thus advisable to analyse at least duplicates.

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