



TXRF analytical methodologies and sample preparation procedures for ultra-trace elements analysis

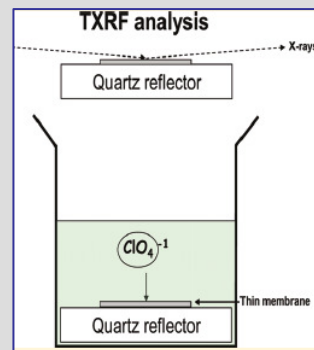
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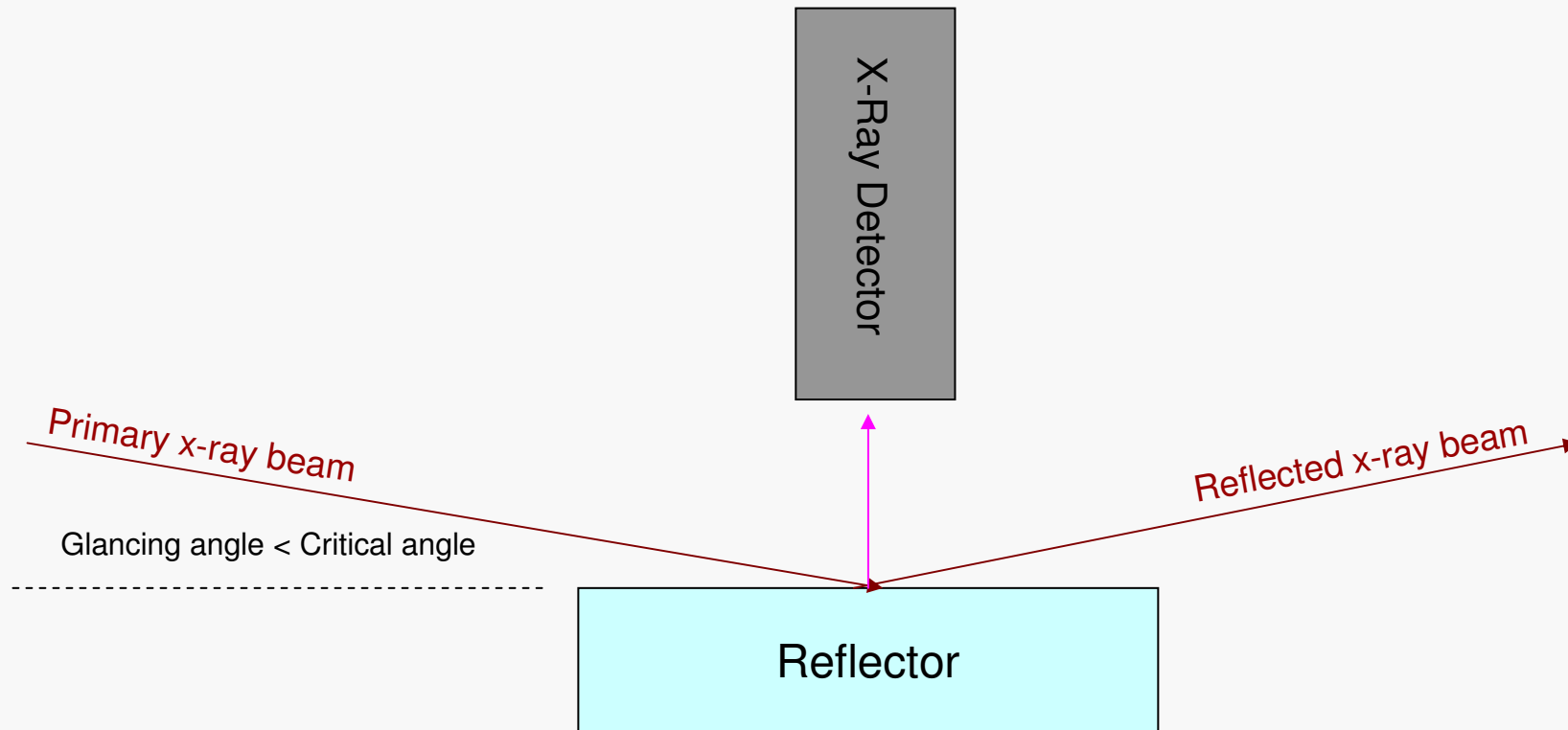


Structure of the presentation

- 1) General Remarks
- 2) Membrane Deposition on Reflector Surface
- 3) Reagent Immobilization on TXRF Reflector Surface
- 4) Membrane Analysis Applications
- 5) TXRF – Reagent Immobilization Analysis

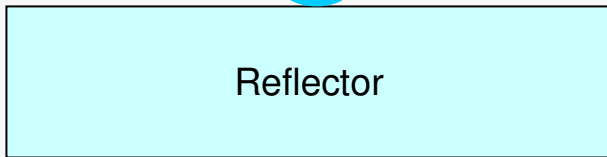


Total Reflection X-ray Fluorescence (TXRF)

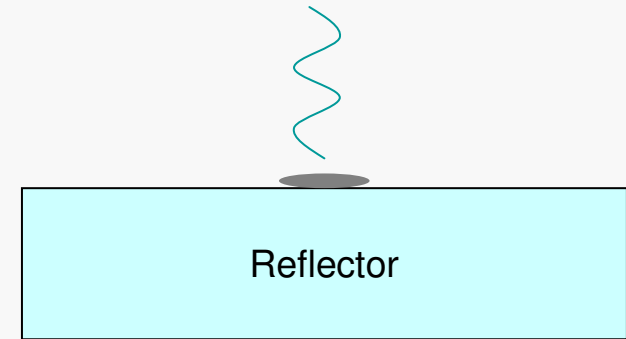




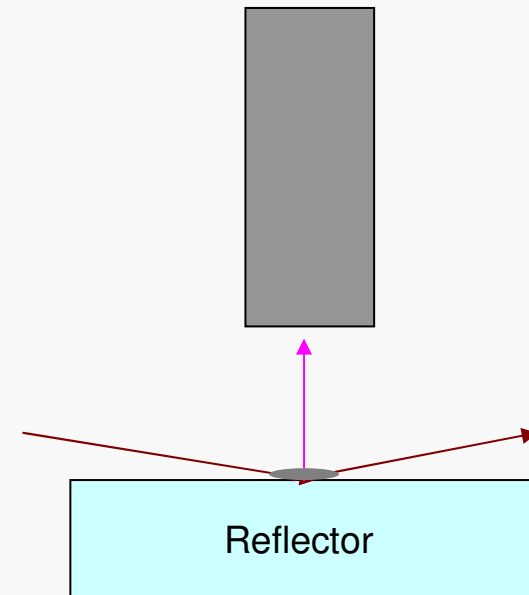
TXRF – liquid analysis



Step 1 – deposition of a liquid drop
(a few μL)



Step 2 – liquid evaporation



Step 3 – TXRF analysis



One of the most important advantages of X-Ray Analysis:

- The possibility of direct analysis of solid samples

Two of the most important disadvantages of X-Ray Analysis:

- The inability to determine chemical species
- Although the Minimum Detection Limits usually are very good for solid sample analysis, they often are inadequate for liquid analyses

Questioning:

Is it possible to overcome the disadvantages by taking advantage of the possibility of solid analysis?

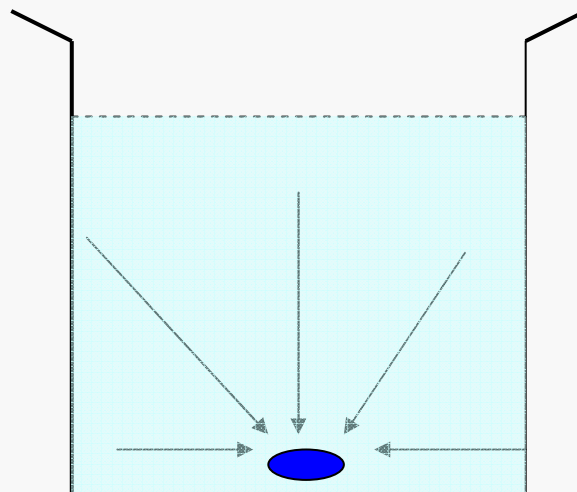


Preconcentration (definition) in trace analysis

An operation (process) as a result of which the ratio of the concentration or the amount of microcomponents (trace constituents) and macrocomponents (matrix) increases. The term enrichment is not recommended.

IUPAC Gold Book

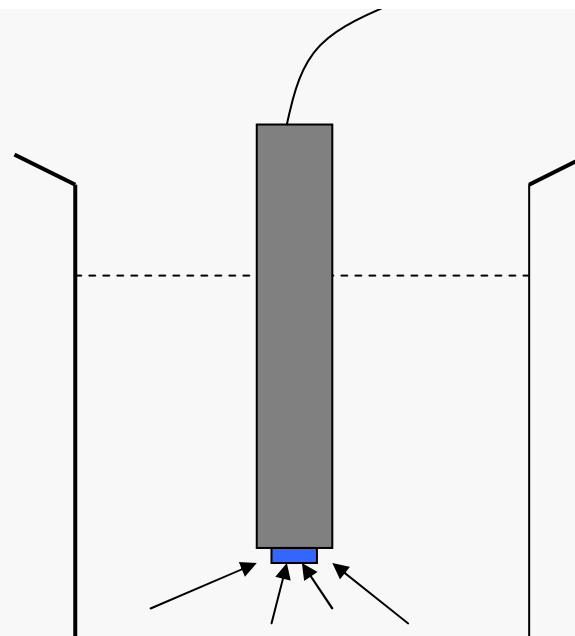
<http://goldbook.iupac.org/P04803.html>





Ion selective electrodes / Chemical Sensors

An electrochemical sensor, based on selective membranes as recognition elements



Membrane-introduction mass spectrometry (MIMS),

Nicholas G. Davey, Erik T. Krogh, Chris G. Gill, Trends in Analytical Chemistry, Vol. 30, No. 9, 2011

MIMS uses a semi-permeable membrane between sample and mass spectrometer. The membrane extracts and preconcentrates analytes providing increased sensitivity.

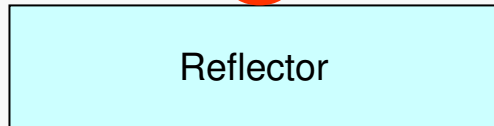


2) Membrane Deposition on Reflector Surface

(an alternative way for TXRF sample preparation)

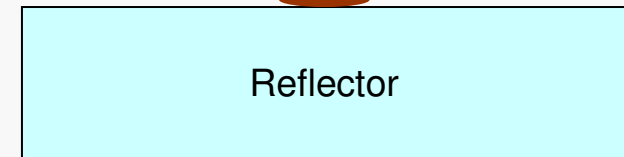


TXRF – Membrane analysis

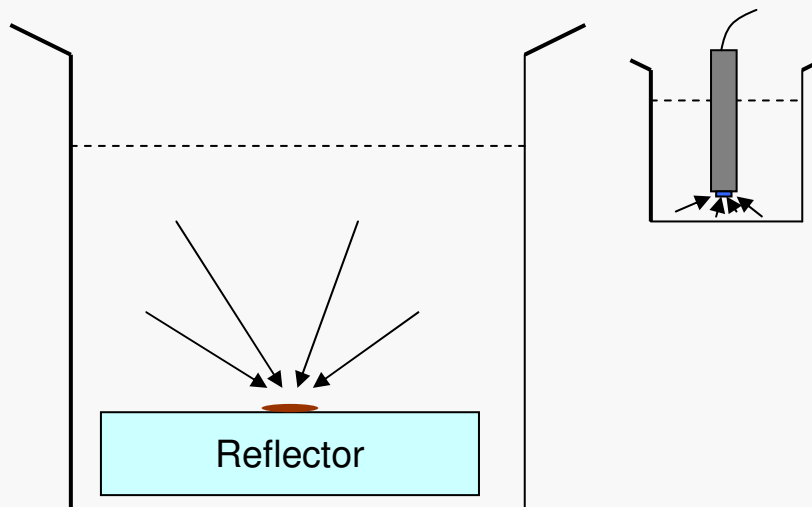


Step 1 – Membrane preparation and deposition of a few μL liquid drop (membrane components in suitable solution)

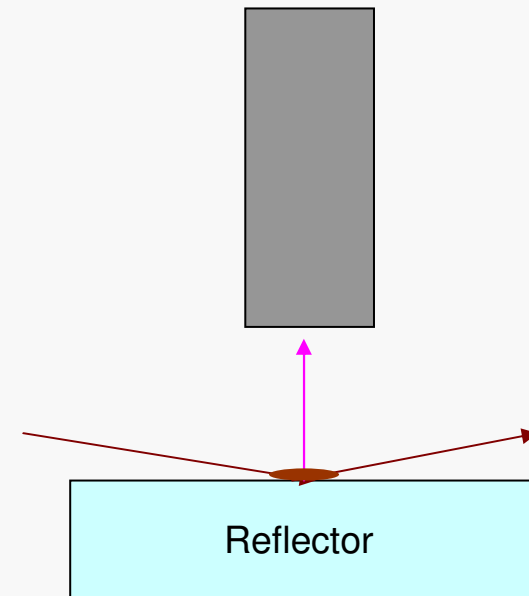
(Air, Oven, IR lamp)



Step 2 – Solvent evaporation



Step 3 – Reflector immersion in the analyzed solution (selective preconcentration)



Step 4 – TXRF (or EDXRF) analysis



Membrane Solution preparation

1) Membrane Matrix Solution

1.1 Membrane polymer: e.g. PVC

1.2 Plasticizer (to improve polymer properties like flexibility): e.g. dibutyl phthalate

1.3 Solvent (for matrix and plasticizer dissolution): e.g. tetrahydrofuran (THF)

2) Complexing Reagent Solution (ligand)

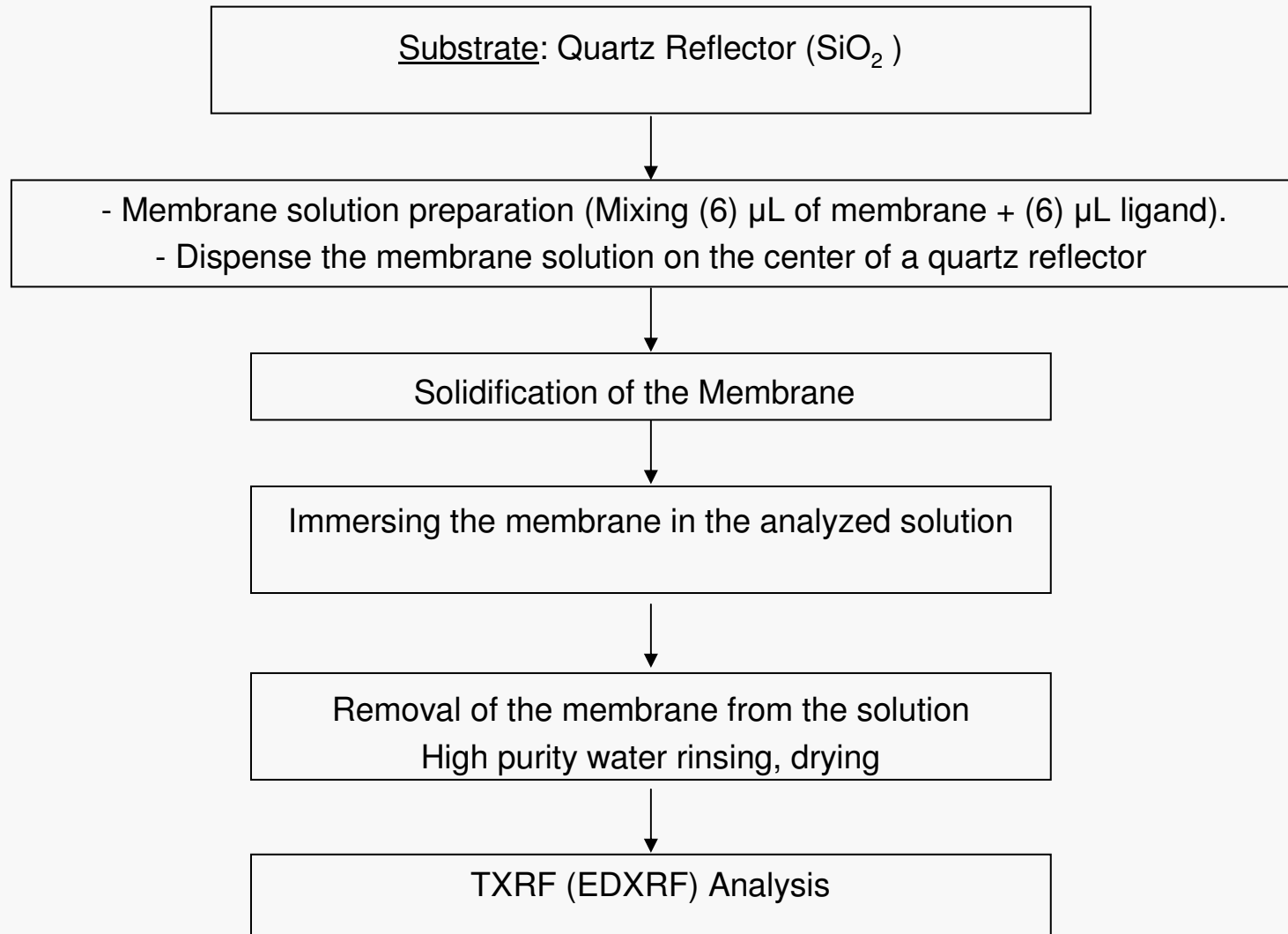
Questions:

- Selection of polymer, plasticizer, ligand?
- Solution Quantitative Composition?
- Membrane mass?
- Analyzed Sample volume?
- pH?
- Temperature?
- Stirring effect?
- Interferences?

etc.

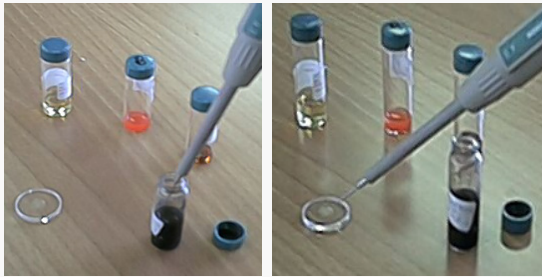


Experimental Procedure





Step 1: Membrane preparation and deposition on a TXRF reflector (or on thin plastic) surface



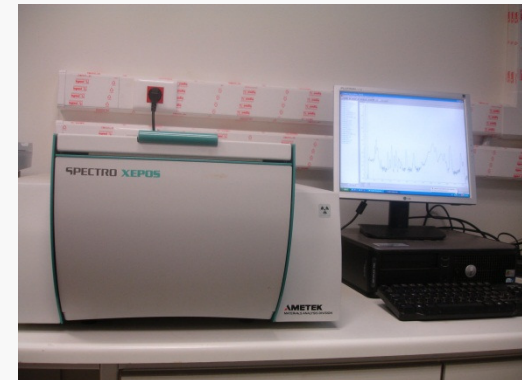
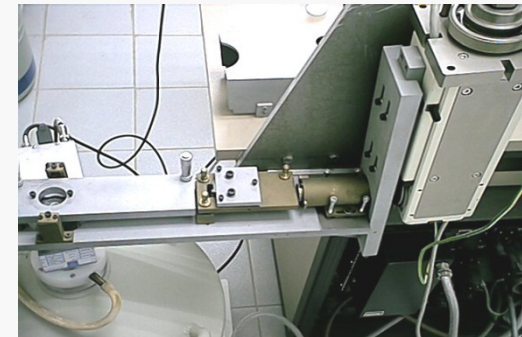
Step 2 – Solvent evaporation



Step 3: reflector immersion in the analyzed solution



Step 4: TXRF (or EDXRF) analysis



Complex formation: A molecular entity formed by loose association involving two or more component molecular entities, or the corresponding chemical species.

Advantage: Extremely high Stability Constants

Questioning: Do complexes keep their properties if they will be introduced in a solid (membrane) matrix?

Titles | New User | Mini-SCDatabase and SolEq | Info on SC-Database | Ligand Structures | User Reporting

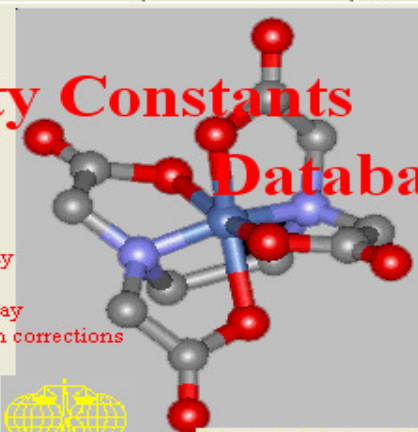
The IUPAC

Stability Constants Database

A database of all significant published metal-ligand stability constants.
with: Speciation curve display
temperature and ionic strength corrections

Academic Software

in cooperation with the
Royal Society of Chemistry



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1992-2000 (software and database)
Structure displays © V. Solov'ev

Academic Software

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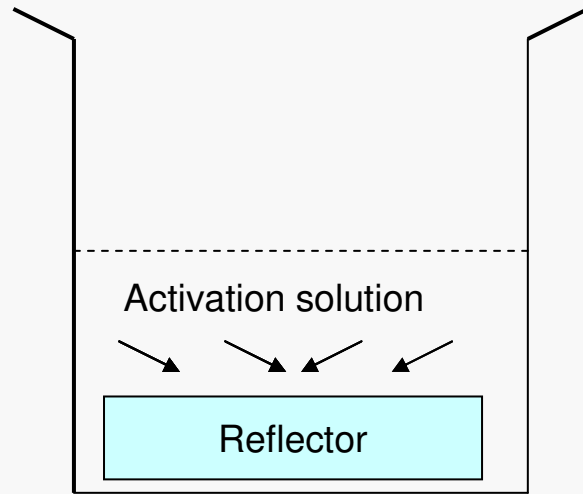


3) Reagent Immobilization on TXRF Reflector Surface

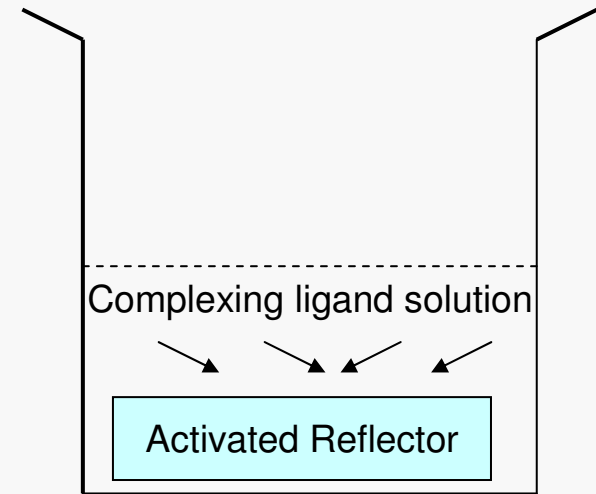
(another way for sample preparation)



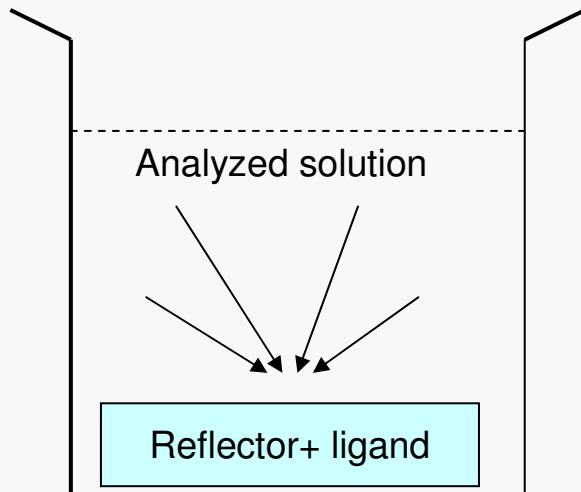
TXRF – Reagent Immobilization analysis



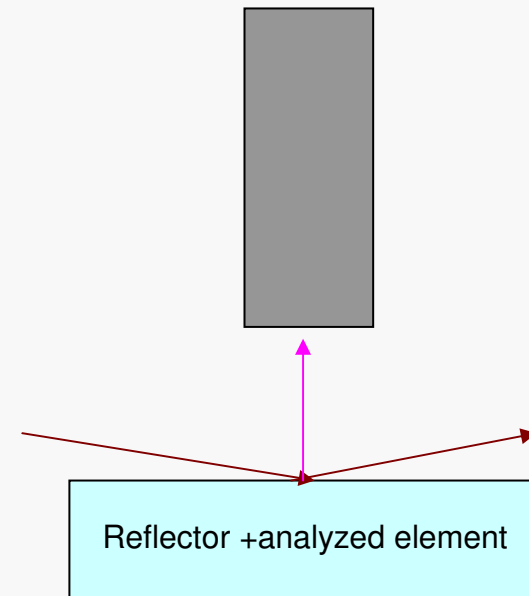
Step 1 – Reflector Activation (in suitable Reagent)



Step 2 – Complexing ligand immobilization



Step 3 – Reflector immersion in the analyzed solution (selective preconcentration)



Step 4 – TXRF analysis



4) Membrane Analysis Applications

Cation Analysis

Mercury

Anion Analysis

Perchlorate

Bromate

Cation + Anion Analysis

Chromium

5) TXRF – Reagent Immobilization Analysis



4) Membrane Analysis Applications

Cation Analysis

Mercury

Anion Analysis

Perchlorate

Bromate

Cation + Anion Analysis

Chromium

5) TXRF – Reagent Immobilization Analysis



Membrane analysis - Mercury

Anal. Chem. 2004, 76, 4315–4319

Selective Mercury Determination after Membrane Complexation and Total Reflection X-ray Fluorescence Analysis

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Analytica Chimica Acta 809 (2014) 25–29



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Contents lists available at [ScienceDirect](#)

Analytica Chimica Acta

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X-ray fluorescence mercury determination using cation selective membranes at sub-ppb levels

Vasilios S. Hatzistavros, Nikolaos G. Kallithrakas-Kontos*

Technical University of Crete, Analytical and Environmental Chemistry Laboratory, GR-73100 Chania, Greece



Membrane composition

Polymeric Ion Selective Membranes Consists of :

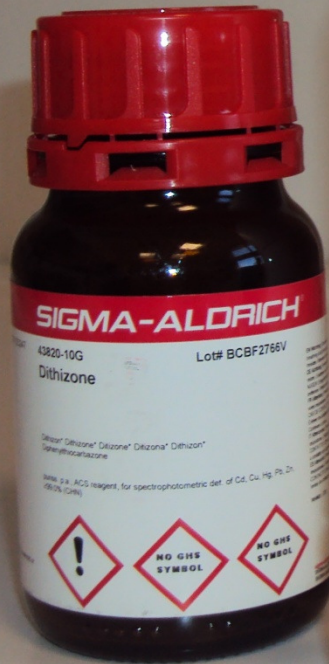
- polymer **matrix** PVC (Polyvinyl Chloride).
- Membrane solvents (**plasticizers**) –dibutyl Phthalate.
- Active components such as **ionophores** - 5,5'-Dithiobis(2-nitrobenzoic acid) (organic compound that facilitates the ion transport across the membrane)
- Selective membranes containing a few micrograms of various **complexing reagents (dithizone)**.
- THF as **Solvent**



Polymer Matrix

Solvent

Complexing Reagent (Ligand)

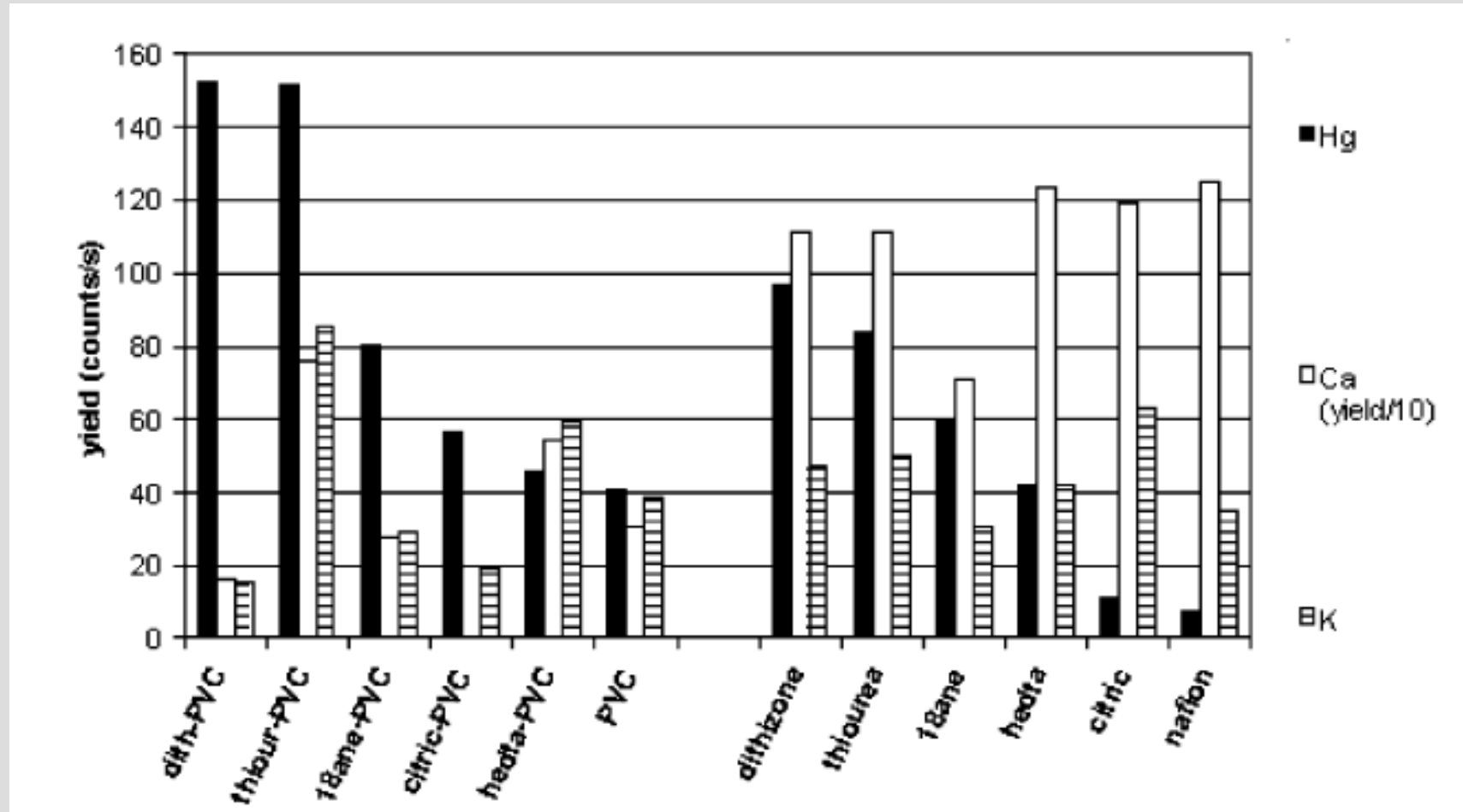


Plasticizer

Ionophore



Complexing ligand selection





Time – (Reflector TXRF)

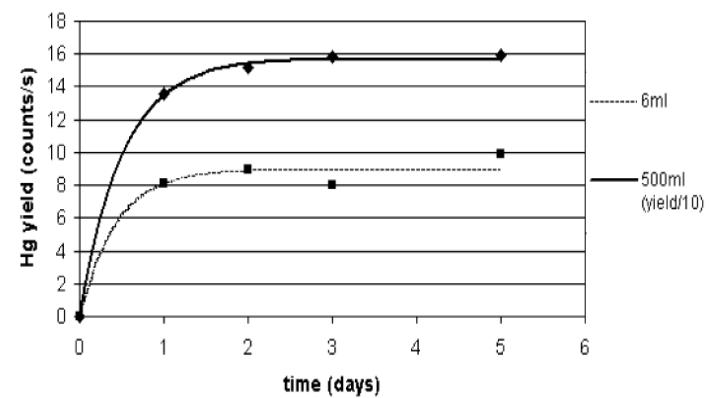
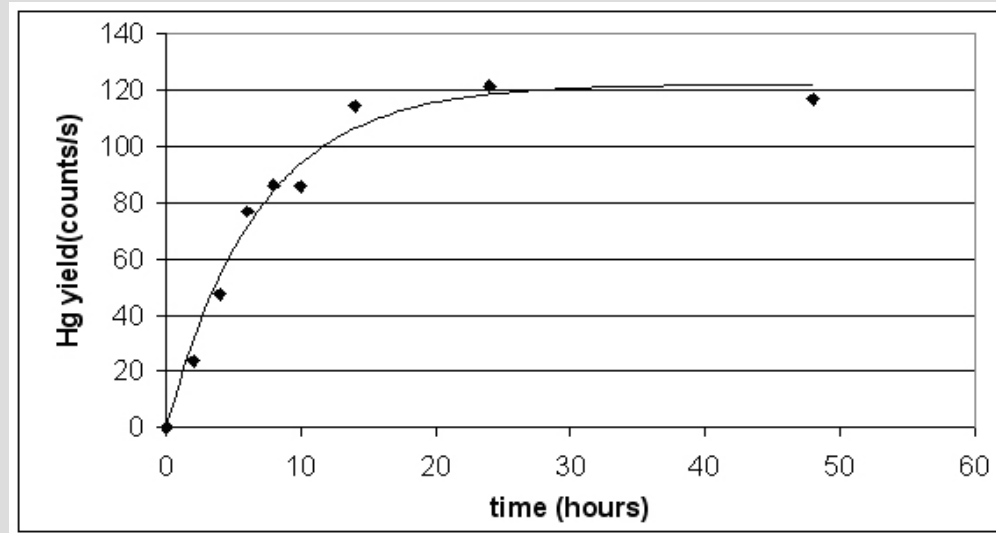


Figure 3. Mercury X-ray yields as a function of equilibration time (Hg concentration 10 ng/mL, PVC–dithizone membrane, solution volume 500 and 6 mL). The 500-mL solution yields have been divided by 10 for better presentation in the same figure.



Time (thin Mylar)

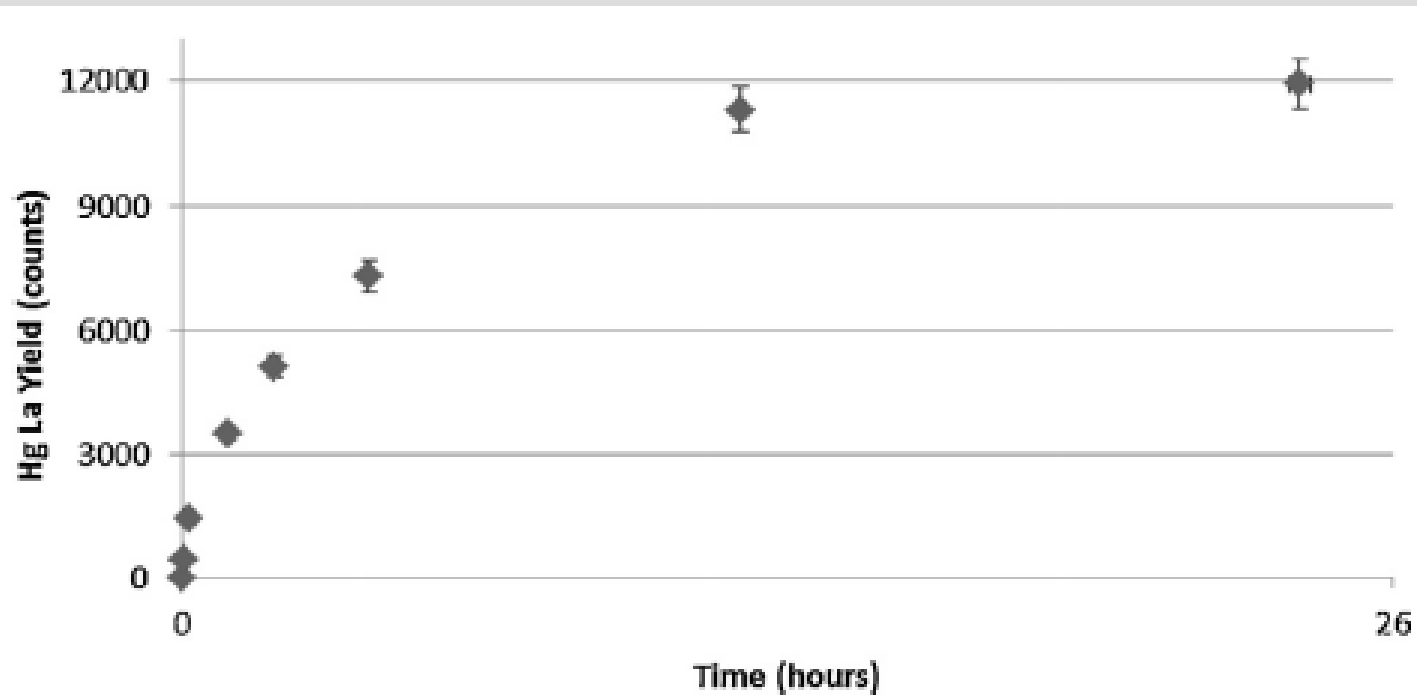


Fig. 2. Mercury X-ray yield as a function of the membrane equilibration time (mercury concentration 25 ng mL^{-1} , irradiation time 300 s, sample volume 1000 mL, room temperature 25°C membrane 2 from Table 1).



Sample volume (TXRF)

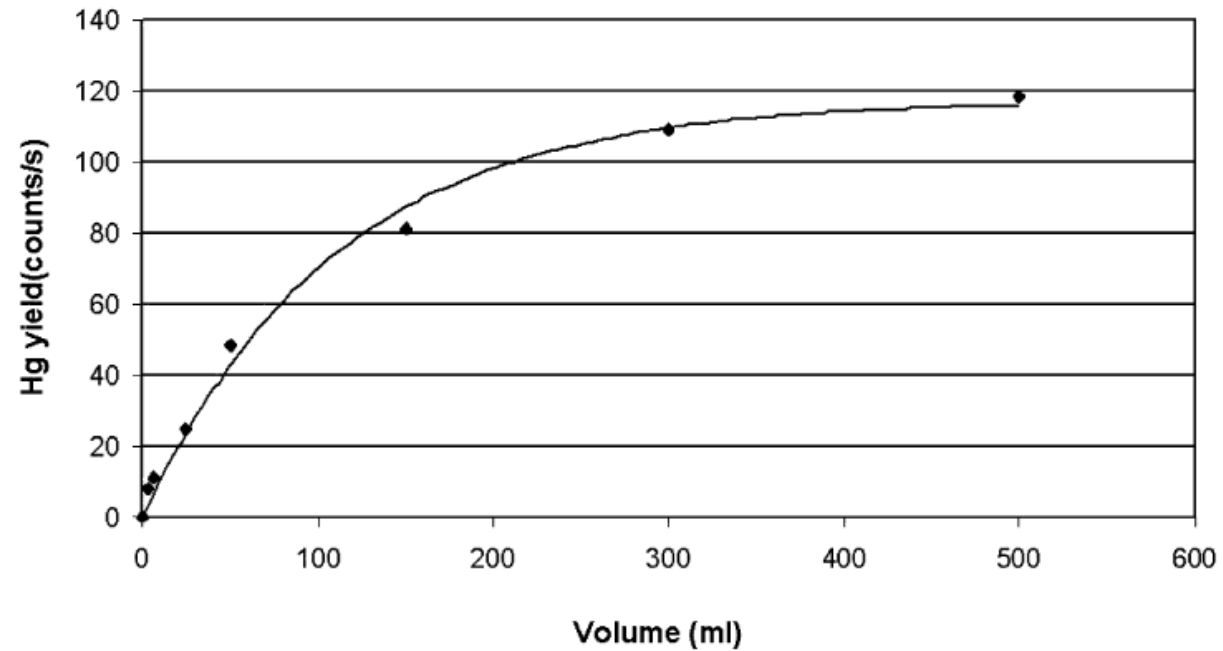


Figure 2. Effect of solution volume on mercury yield (Hg concentration 10 ng/mL, PVC–dithizone membrane, equilibration time 24 h). Linearity exists up to 50 mL of solution volume.



Sample volume (thin Mylar)

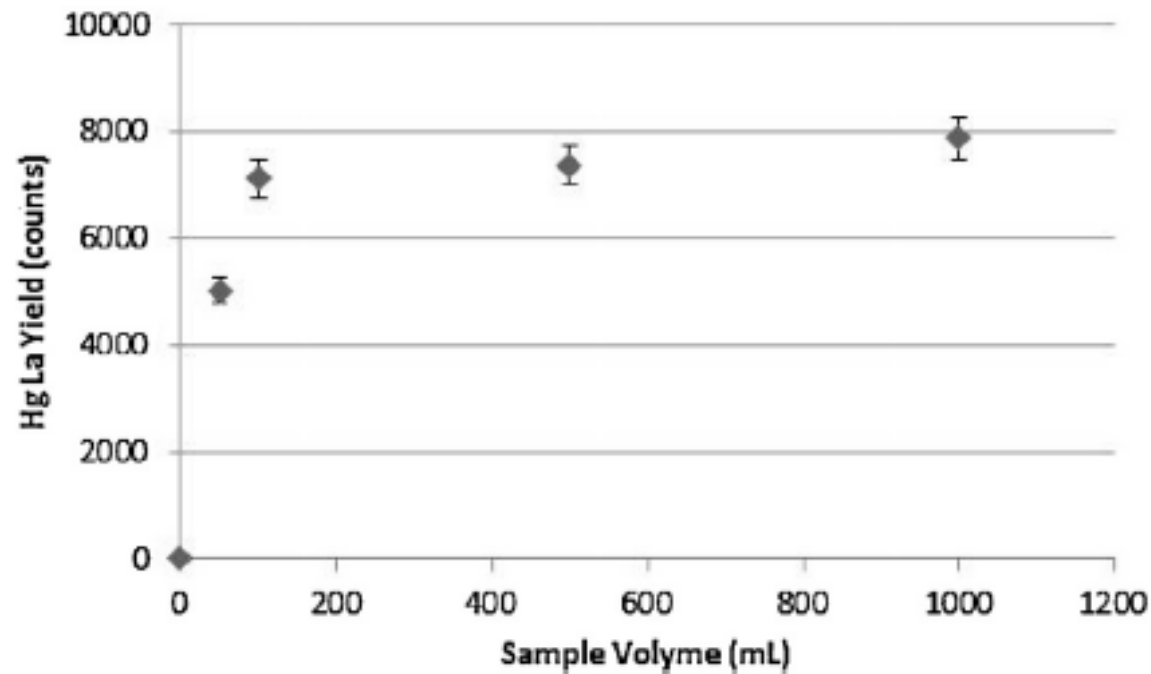
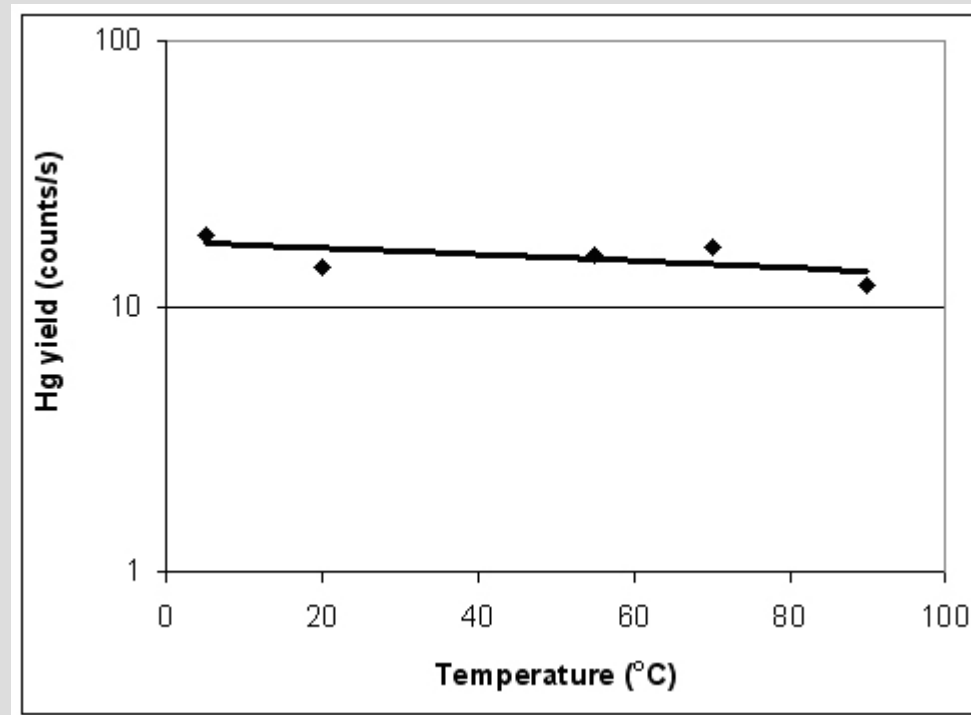


Fig. 3. The effect of the sample volume in the collected mercury yield (mercury concentration 25 ng mL^{-1} irradiation time 300 s, room temperature 25°C).

Temperature



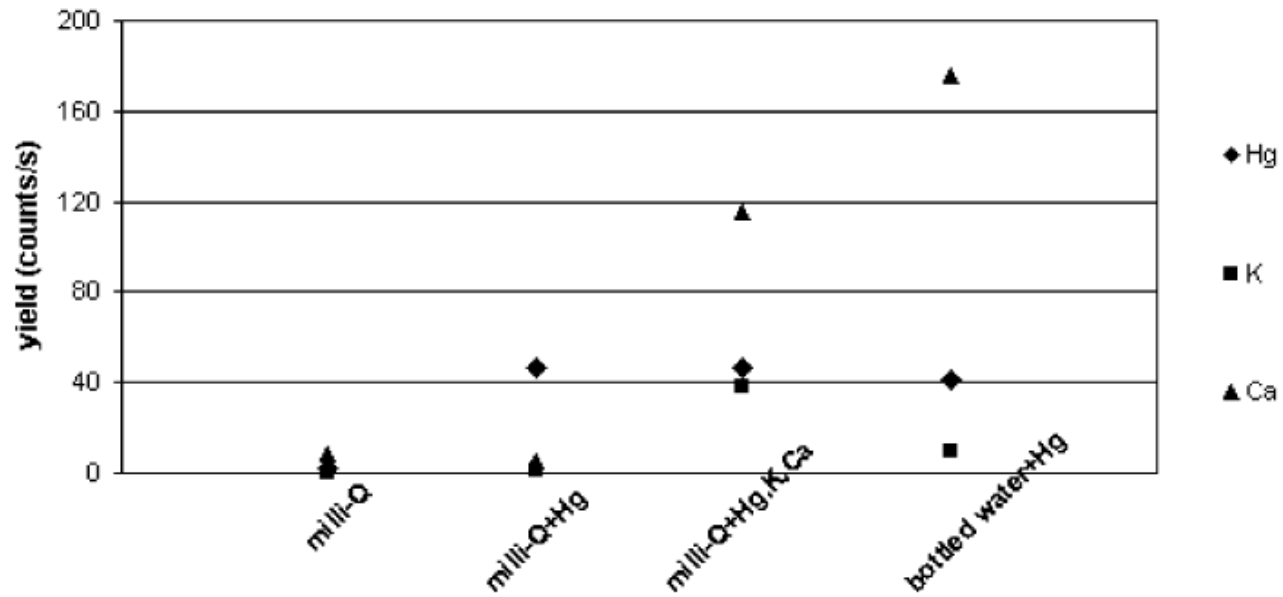


Figure 4. Influence of potassium and calcium ions on mercury yields (Hg concentration 10 ng/mL, PVC–dithizone membrane, equilibration time 24 h, solution volume 50 mL) for four different solutions.

50 mg/L Calcium, 5 mg/L K

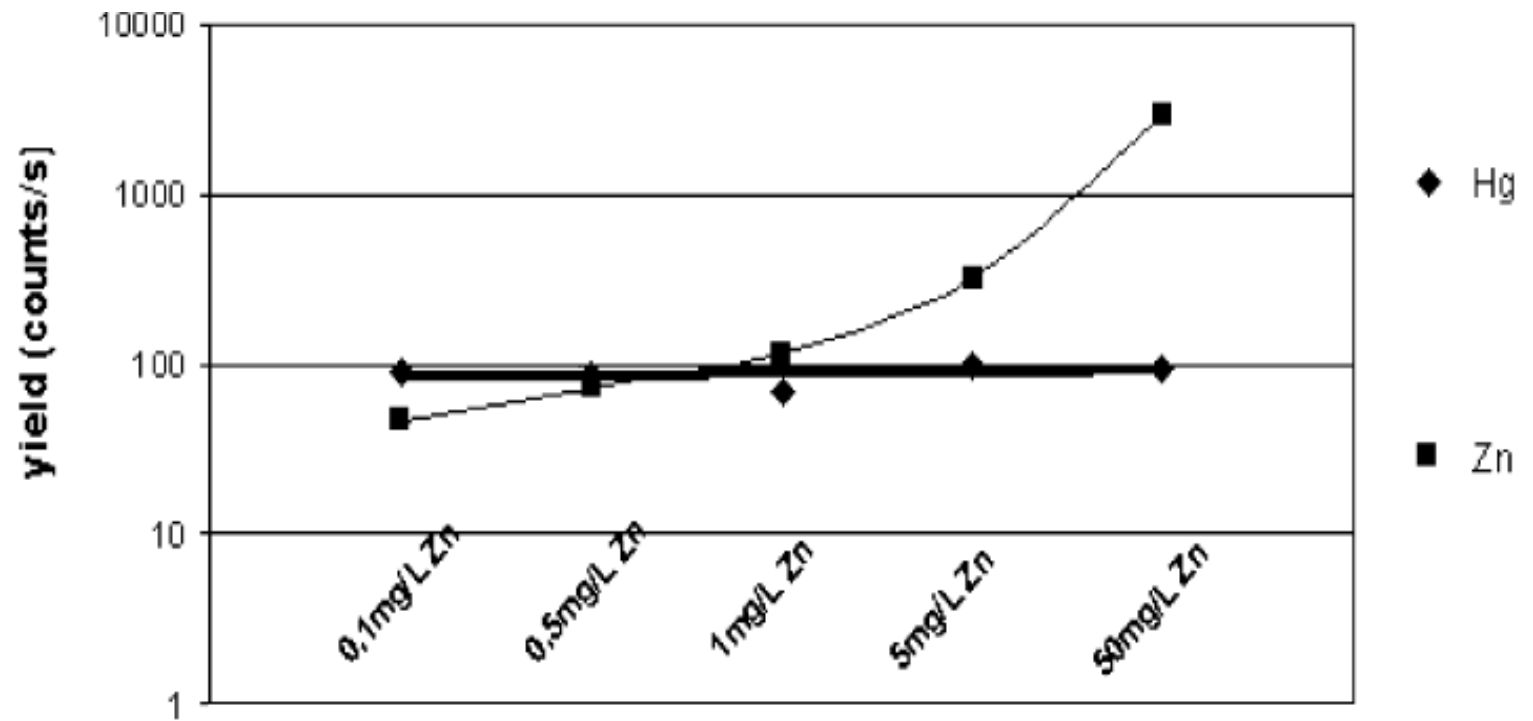
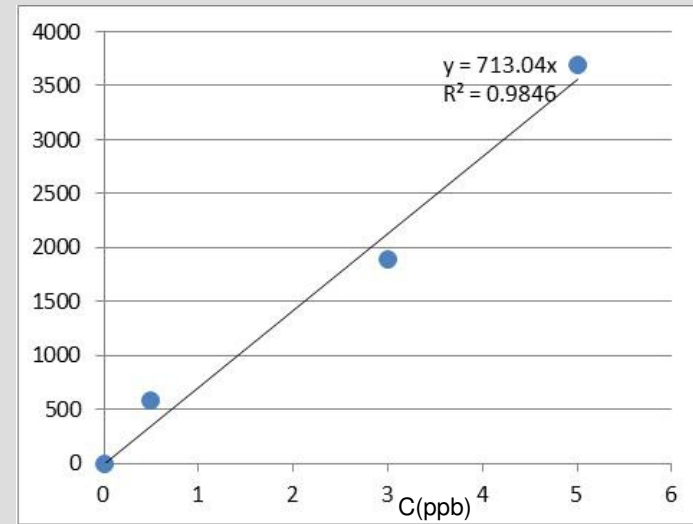
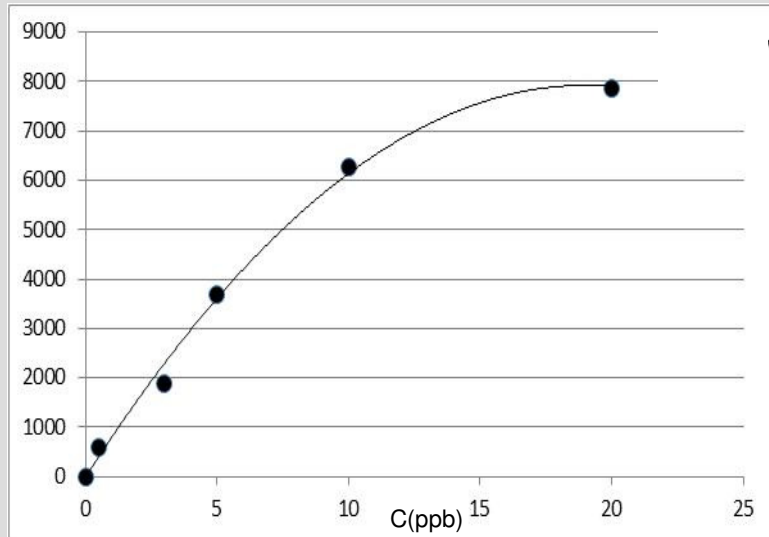


Figure 5. Mercury yields as a function of the zinc concentration in the solution.

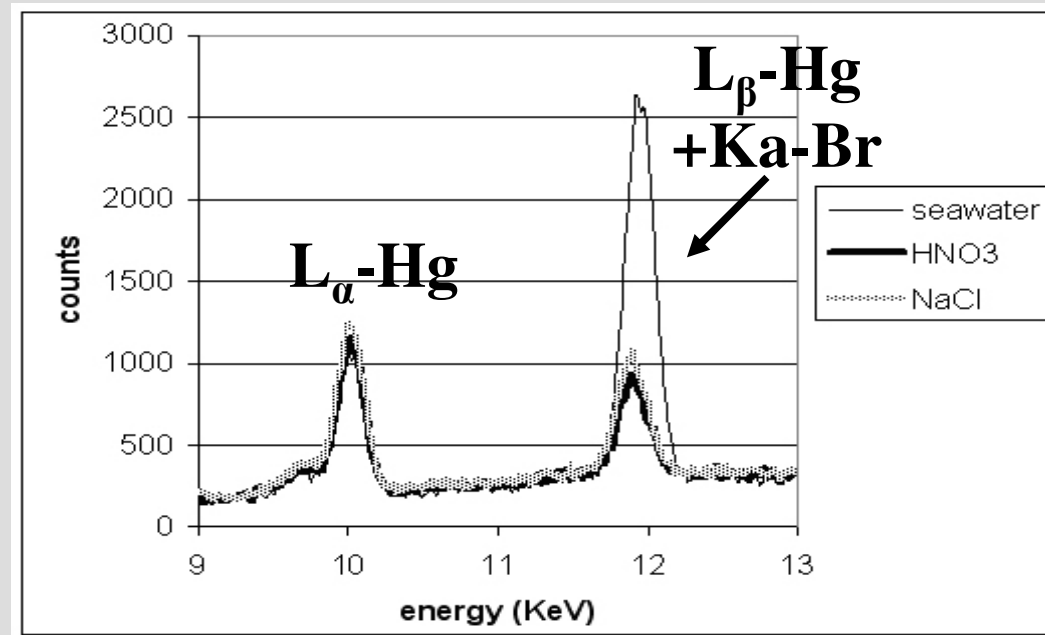


Linearity (seawater)





Spectra Comparison



(In seawater spectrum, Br- K_{α} line overlaps with Hg- L_{β})

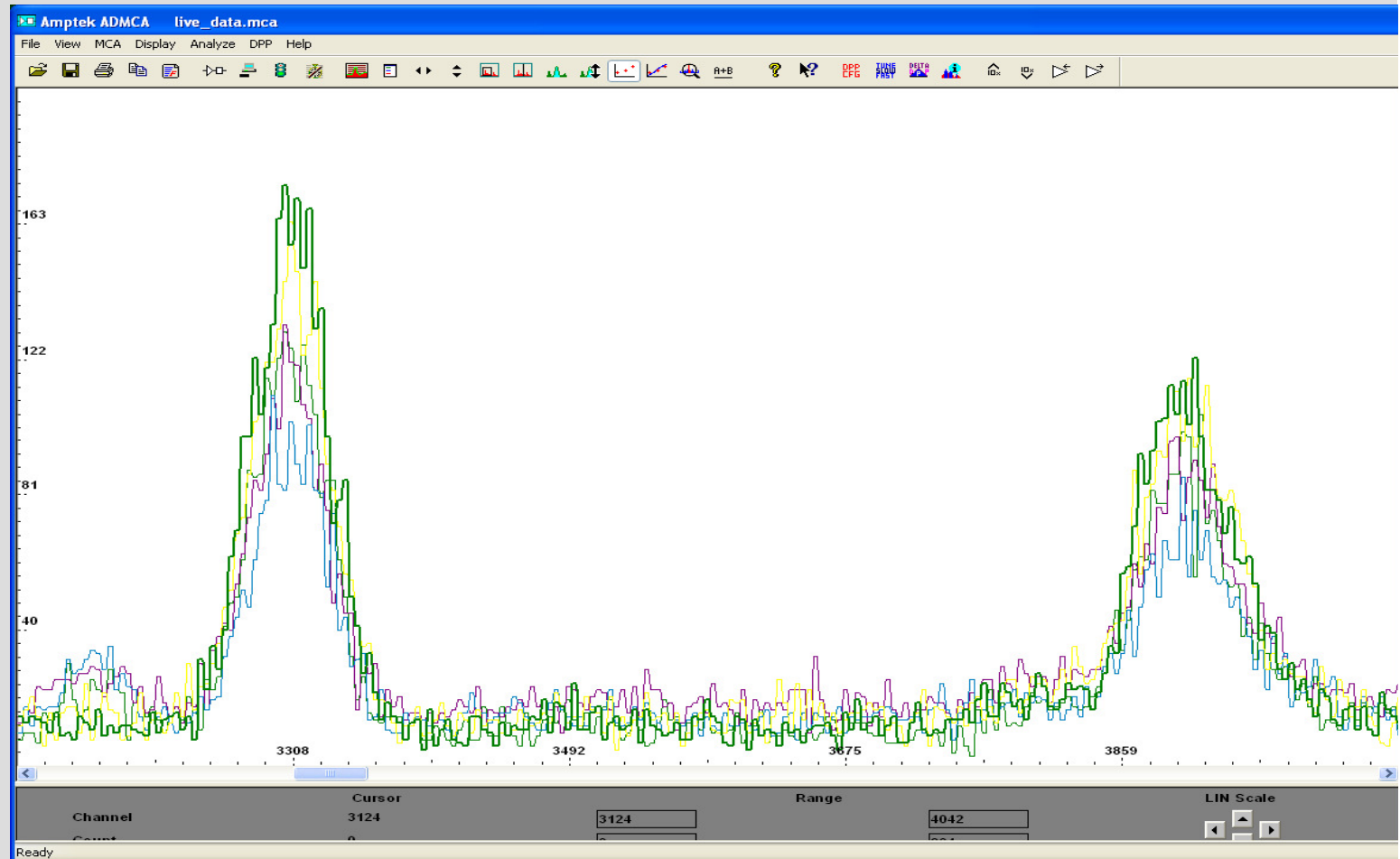
- HNO₃ → Drinking Water, with pH adjusted to zero (0) by HNO₃
- NaCl → Milli-Q water + 60 g/L NaCl (similar to seawater)
- MDL 0.2 ppb (drinking water), 0.4 ppb (seawater)



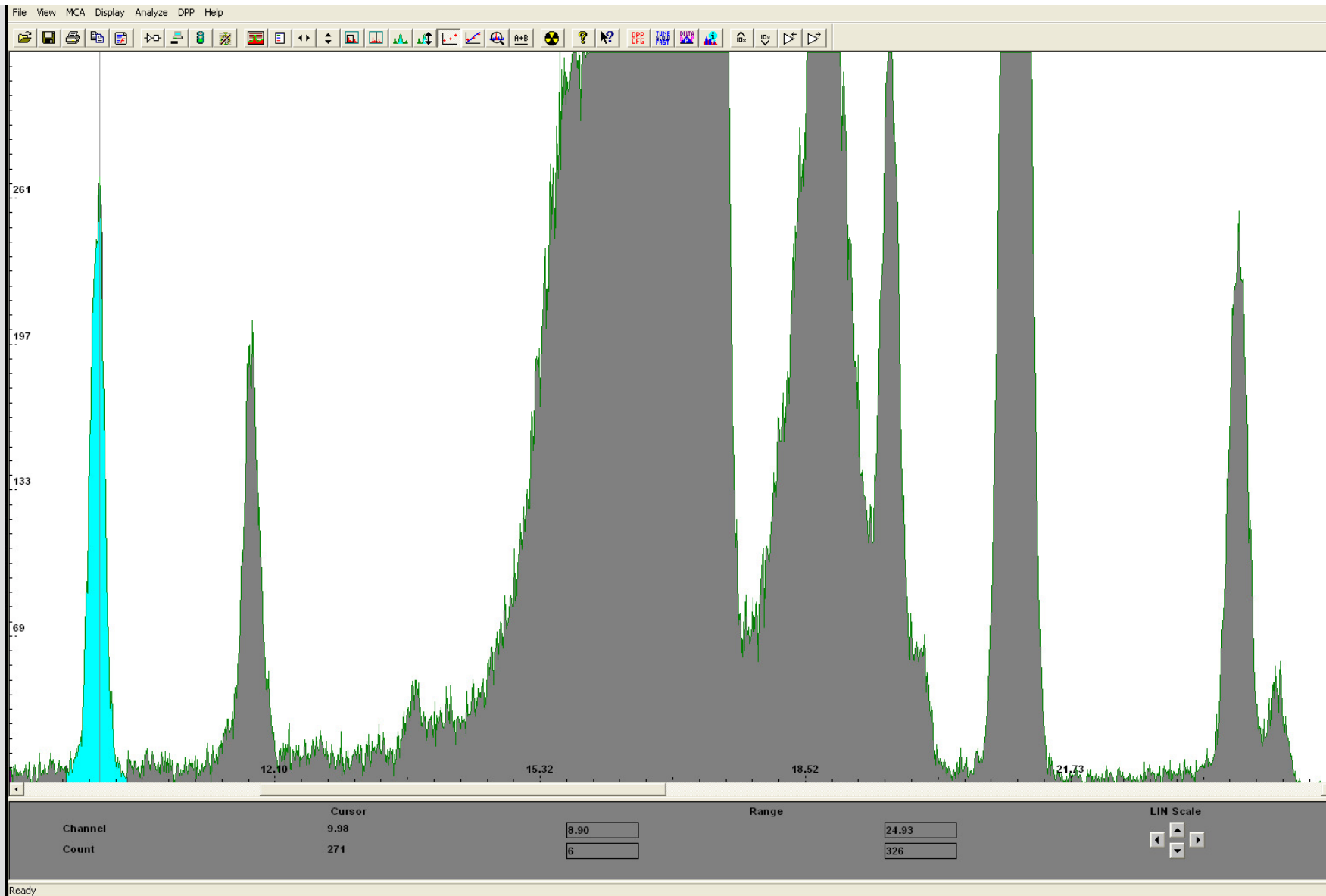


<u>Substrate</u>	<u>Spectra line color</u>	<u>Hg Lα</u>
Prolene 4 μm	green	1631
Microporous gas permeable	purple	1285
Mylar 6 μm	blue	1263
Polyimide (Kapton) 7.5 μm	yellow	1998
Mylar 2.5 μm	green thick	2416

Various Substrates (Hg 10 ppb)



Membrane Composition:
35%w/v PVC,
43%w/v Dibutyl phthalate,
9%w/v Ionophore,
13 % w/v Dithizone



EDXRF analysis -15 ppb Hg (commercial instrument)

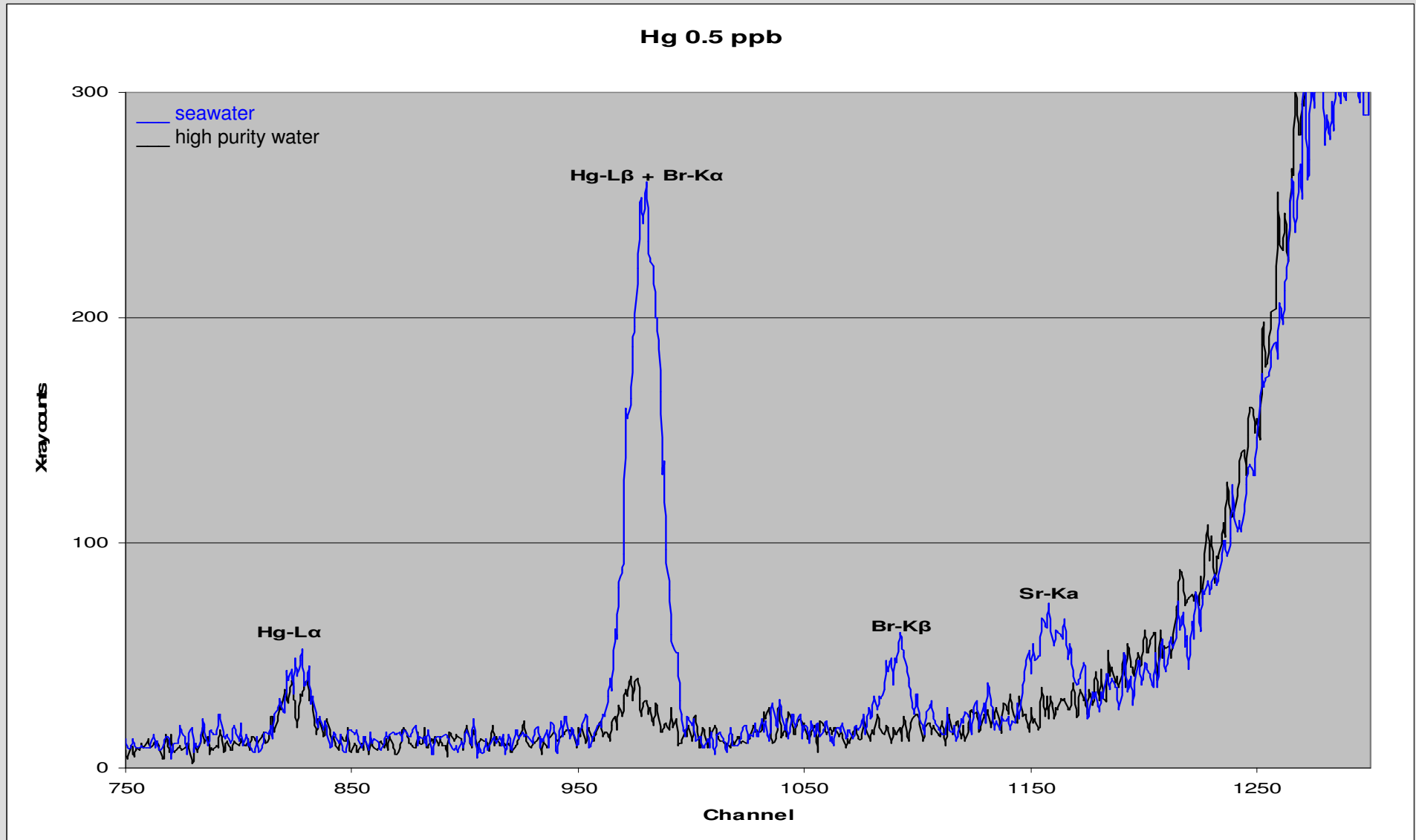


Minimum Detection Limits

Minimum detection limits for 300 s irradiation time

Seawater: 0.064 $\mu\text{g/L}$ (64 ppt)

High purity water (18 M Ω): 0.069 $\mu\text{g/L}$ (69 ppt)





Membrane Analysis Applications

Cation Analysis

Mercury

Anion Analysis

Perchlorate

Bromate

Cation + Anion Analysis

Chromium



TXRF – Reagent Immobilization Analysis



Anion Analysis - Perchlorate

analytical
chemistry

ARTICLE

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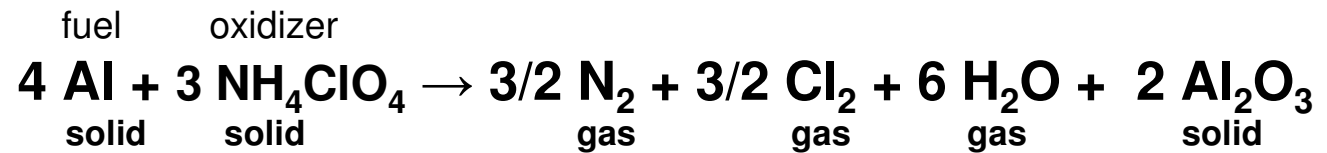
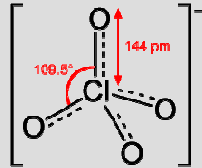
Determination of Trace Perchlorate Concentrations by Anion-Selective Membranes and Total Reflection X-ray Fluorescence Analysis

Vasilios S. Hatzistavros and Nikolaos G. Kallithrakas-Kontos*

Analytical and Environmental Chemistry Laboratory, University Campus, Technical University of Crete, GR-73100 Chania, Greece



Perchlorate Analysis



High redox potential, high oxygen content but slow reaction unless heated. Rough mass proportions 70% ammonium perchlorate/ 15% hydroxyl-terminated polybutadiene HTPB / 15% Al

Other perchlorate applications/presence

- ✓ Airbags (oxidizer)
- ✓ Bleaches
- ✓ Fireworks (oxidizer)
- ✓ Byproduct of chlorine generators (in swimming pool chlorination systems)

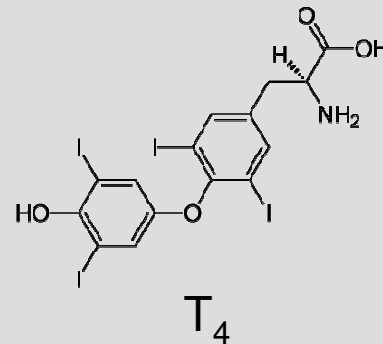
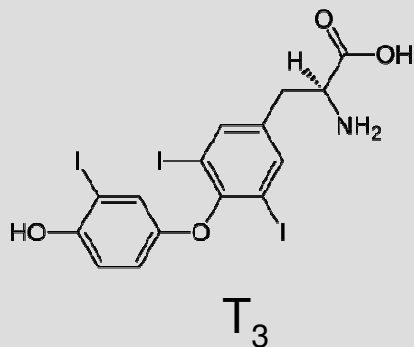
- ✓ Fertilizers (naturally occurring)



Safety problems

- Thyroid uses Iodine for hormone production
- Perchlorate has similar properties and size with Iodine
- “High” perchlorate concentrations interfere with Iodine and block its absorption in thyroid (hypothyroidism)_(it has been used in the medicine to treat hyperthyroidism)

Thyroid selectively absorbs Iodine (I^-). Iodine (and tyrosine) are used to form:
Triiodothyronine (T₃) and Thyroxine (T₄)



T₃ and T₄ affect growth, metabolism, body temperature, heart rate etc.



Technical Fact Sheet – Perchlorate

January 2014



TECHNICAL FACT SHEET – PERCHLORATE

Perchlorate is highly soluble in water, and relatively stable and mobile in surface and subsurface aqueous systems. As a result, **perchlorate plumes in groundwater can be extensive**. For example, the perchlorate plume at a former safety flare site (the Olin Flare Facility) in Morgan Hill, California, extends **more than 9 miles**

High concentrations of perchlorate have been detected primarily at current and Formerly Used Defense Sites historically involved in the manufacture, testing and disposal of ammunition and rocket fuel or at industrial sites where perchlorate is manufactured or used as a reagent during operations ... **it is generally difficult to identify specific military sites with known perchlorate releases. From 1997 to 2009, the Department of Defense reported perchlorate detections at 284 (almost 70 percent) of its installations sampled**

The EPA established an Interim Lifetime Drinking Water Health Advisory of 15 micrograms per liter (µg/L), which is a concentration of a perchlorate in drinking water that is not expected to cause any adverse noncarcinogenic effects for a lifetime of exposure (EPA 2009, 2012a).



Technical Fact Sheet – Perchlorate

January 2014



TECHNICAL FACT SHEET – PERCHLORATE

EPA calculated a tap water screening level of 11 µg/L for perchlorate and perchlorate salts (EPA 2013).

EPA has calculated a **residential soil screening level (SSL) of 55 milligrams per kilogram** (mg/kg) and an industrial SSL of 720 mg/kg for perchlorate and perchlorate salts (ammonium, potassium, sodium and lithium) (EPA 2013).

Numerous states have promulgated enforceable standards for perchlorate in drinking water. For example, **Massachusetts (2 µg/L) and California (6 µg/L)** have established enforceable standards for perchlorate in drinking water (CDPH 2012; Massachusetts DEP 2006).

At least 10 other states have also developed advisory levels or health-based goals for perchlorate, ranging from 1 to 18 µg/L for drinking water and 1 to 72 µg/L for groundwater (GAO 2010).

Breaking News

Perchlorate in drinking water more detrimental to infants than expected: study

(philstar.com) Updated December 12, 2010 01:01 PM Comments (0)

LOS ANGELES (Xinhua) - Infants who drink water containing low levels of the chemical perchlorate face a greater health risk than previously believed, a new study suggests.

In the study, researchers looked at ground drinking water slightly contaminated with perchlorate in several cities in Southern California, the Press Enterprise said Saturday.

The study shows that infants who drank water slightly contaminated with perchlorate had a 50-percent chance of developing poorly performing thyroid glands, the paper said, quoting Dr. Craig Steinmaus from California's Office of Environmental Health Hazard Assessment (OEHHA) and lead author of the study.

HEALTH

EPA Wants to Limit Perchlorate in Drinking Water

Published February 02, 2011 | Fox News Latino

Perchlorate cleanup could start in summer

March 19, 2012 4:39 PM

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[SAM PEARSON, staff writer](#)

BARSTOW • Clean up of the source of perchlorate contamination in soil and groundwater in Barstow likely will not begin until June, officials say. Earlier estimates had put the start date as early as February.

The Lahontan Regional Water Quality Control Board and U.S. Environmental Protection Agency are working to determine the best methods for cleaning up groundwater and soil contamination that Golden State Water Company first detected in 2010 in wells near the home of the former owner of the Mojave River Pyrotechnics Company.

Starting in Dec. 2010, the EPA sampled soil from 25.5 acres of the former pyrotechnics facility and the owner's nearby residence. They found concentrations at the residence as high as 130,000 milligrams of perchlorate per kilogram of soil, much higher than the allowed level of 55 milligrams per kilogram. Sampling of groundwater showed concentrations of 110,000 micrograms per liter. No contamination was found at the pyrotechnics manufacturing facility.



Du perchlorate d'ammonium dans les zones de captage de l'eau à Bordeaux

19.07.2011

Actualité Région

Perchlorate dans l'eau potable : la Société des Eaux du Nord ferme temporairement une usine de traitement

PUBLIÉ LE 30/09/2011 À 05H23

« C'est une première et c'est une décision lourde à prendre. » Pas franchement ravi, Jean-Christophe



Didio, le PDG de la Société des Eaux du Nord. Mercredi, des analyses ont montré la présence d'ions perchlorate dans plusieurs ressources en eau qui alimentent (entre autres) la métropole lilloise.

Résultat : l'usine de traitement de Flers-en-Escrebieux (près de Douai) a été temporairement fermée hier matin. Elle alimente habituellement un bassin d'environ 145 000 habitants, du sud de la métropole lilloise, de Flers-en-Escrebieux, de Camphin-en-Carembault, d'Ostricourt, Phalempin, Thumeries, Wahagnies, Avelin, Pont-à-Marcq, Évin-Malmaison et Leforest (notre carte). Une solution d'approvisionnement a été trouvée pour les foyers concernés.



April 10, 2014

Environmental Health News

Levels of naturally occurring perchlorate are higher than expected in Nevada's Amargosa desert.



Solution No 1: Test of various membrane composition

Membrane	Membrane Matrix	Matrix % w/w	Plasticizer % w/w	Anion Extractant % w/w	Solvent 5 mL
M1	EVA	60	*	40	THF
M2	EVA	70	*	30	THF
M3	EVA	40	*	60	THF
M4	EVA	50	*	50	THF
M5	CTA	57	14	29	THF
M6	CTA	28	62	10	THF
M7	CTA	50	10	40	THF

*EVA can be without plasticizer as it has itself the suitable mechanical and electrical properties

CTA: cellulose-triacetate

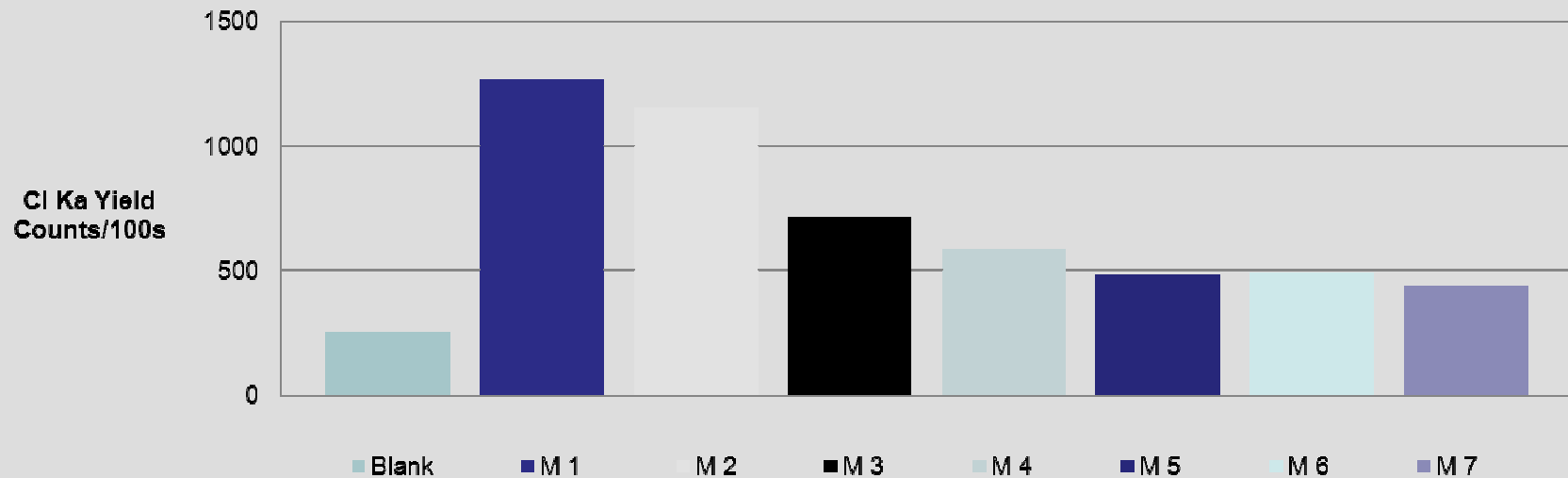
EVA: poly(ethylene-co-vinyl-acetate) copolymer

Anion Extractant: Aliquat-336 = N-Methyl-N,N,N-trioctyl-octan-1-ammonium chloride⁴³
(extractant+plasticizer)



Solution No 1: Test of various membrane matrix composition - Results

Membrane Selection



Perchlorate Concentration: 50ppb

Best Membrane : EVA 60 % w.w , Anion Exchanger Aliquat 40 % w/w

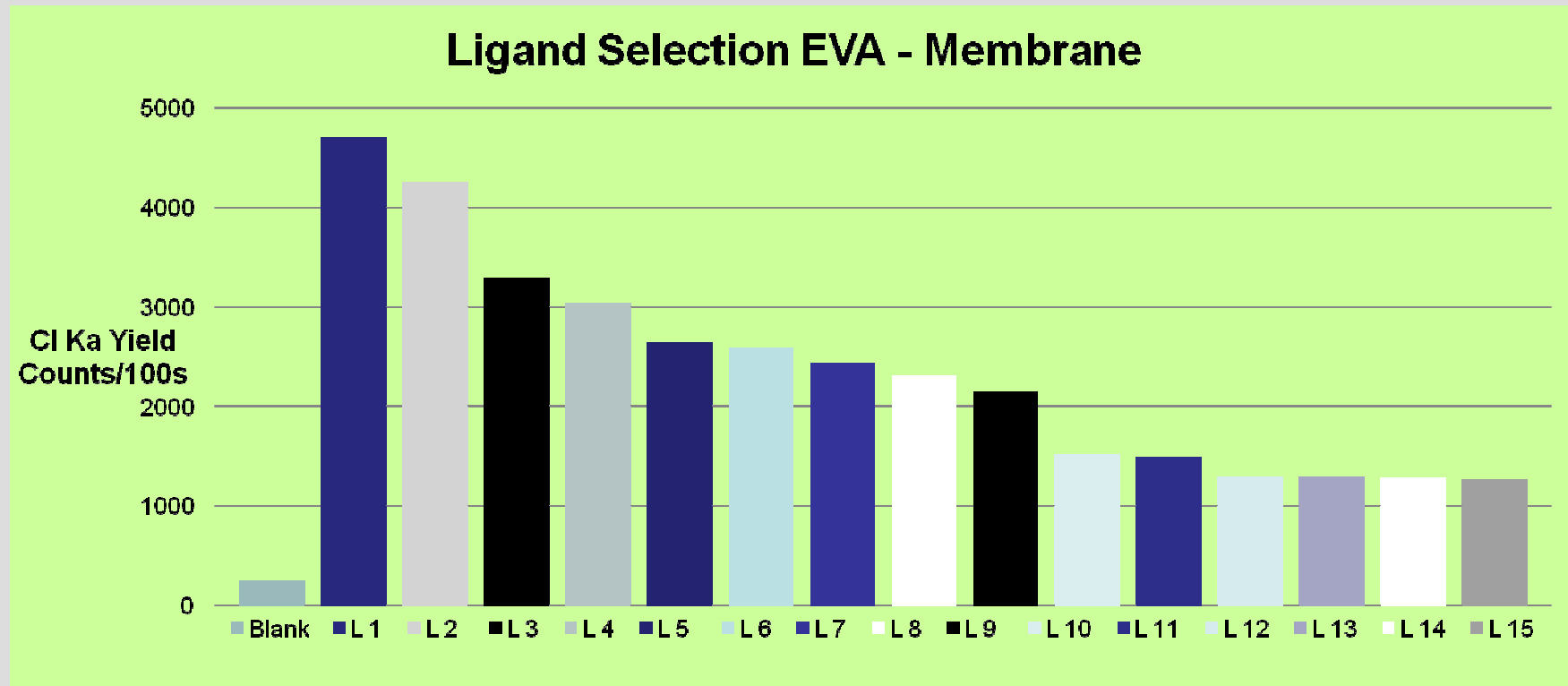


Solution No 2: Chemical reagents (Complexing ligands)

Ligand Number	Ligand
L 1	1- Nitroso-2- Naphthol
L 2	4- Nitrocatechol
L 3	Morin Hydrate
L 4	Antipyrin
L 5	Phenyl Acetate
L 6	o- dianisidin
L 7	Citric Acid
L 8	Thiourea
L 9	TTHA
L 10	Dibenzoylmethane
L 11	Dithizone
L 12	Ammonium pyrrolodinedithiocarbamate
L 13	2- Mercaptobenzothiazole
L 14	4(2- pyridylazo) resorcinol
L 15	HEDTA



Solution No 2: Chemical reagents (Complexing ligands) - Results



Perchlorate Concentration : 50 ng/mL

M1 Membrane + 1- Nitroso-2- Naphthol

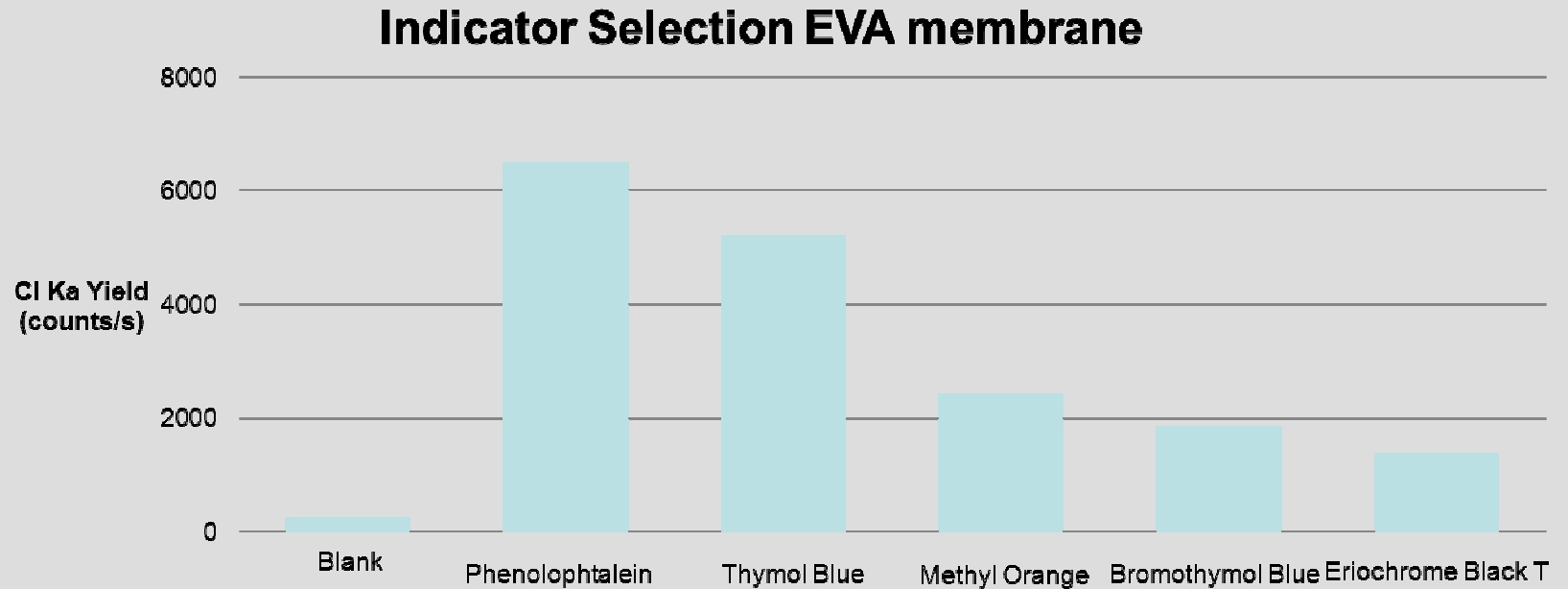


Solution No 2: test of indicator use

Indicators Number	Indicator
I 1	Phenolophtalein
I 2	Thymol Blue
I 3	Methyl Orange
I 4	Bromothymol Blue
I 5	Eriochrome Black T

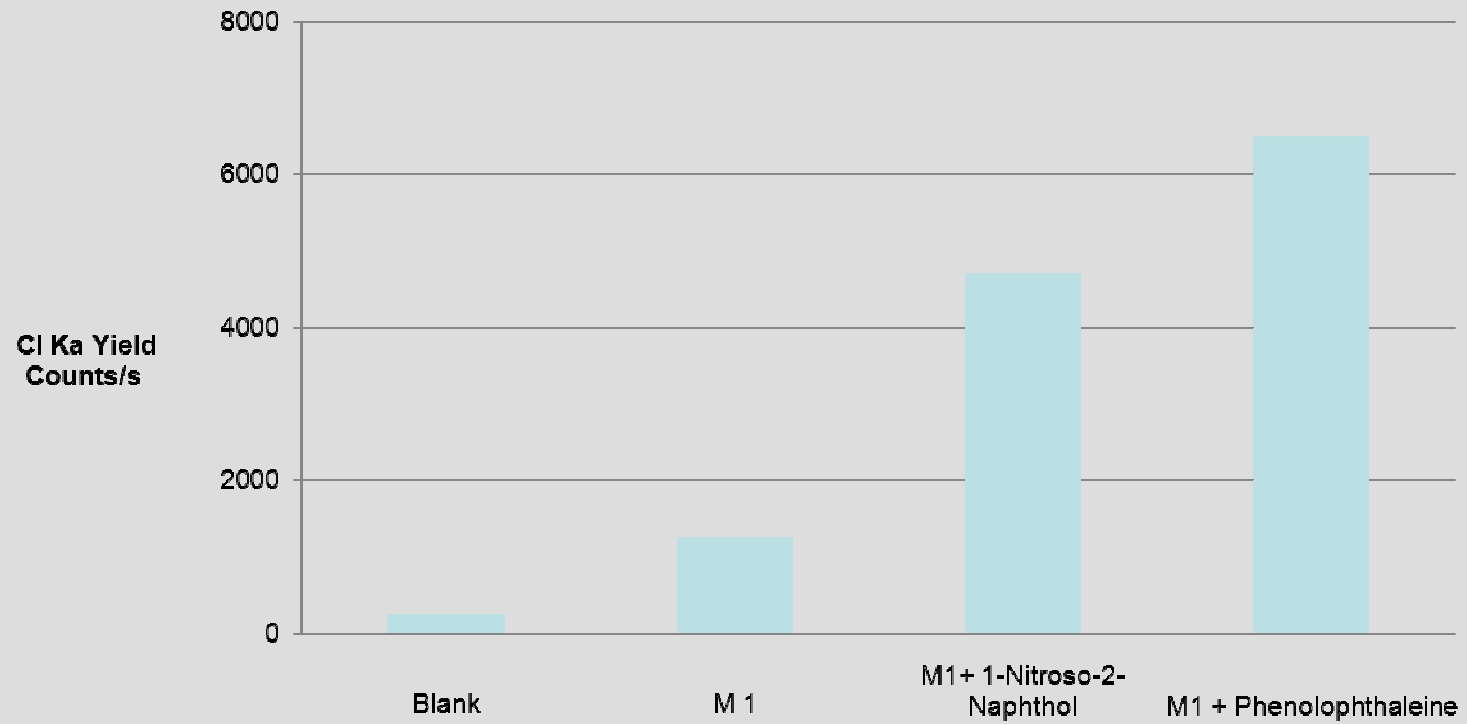


Solution No 2: test of indicator use - Results



Perchlorate concentration : 50 ng/mL

Best composition: M1 membrane +Phenolophtaleine



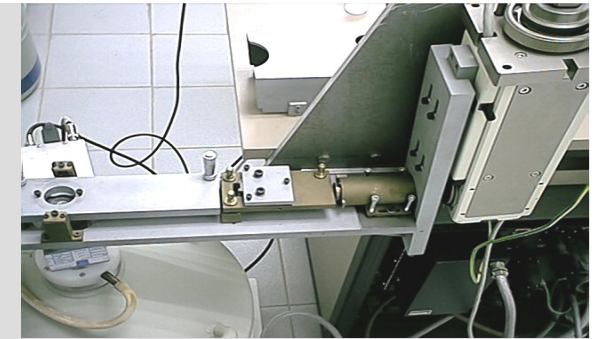
Blank = membrane without perchlorate solution immersion

All the others have been immersed in 50 ppb perchlorate solution

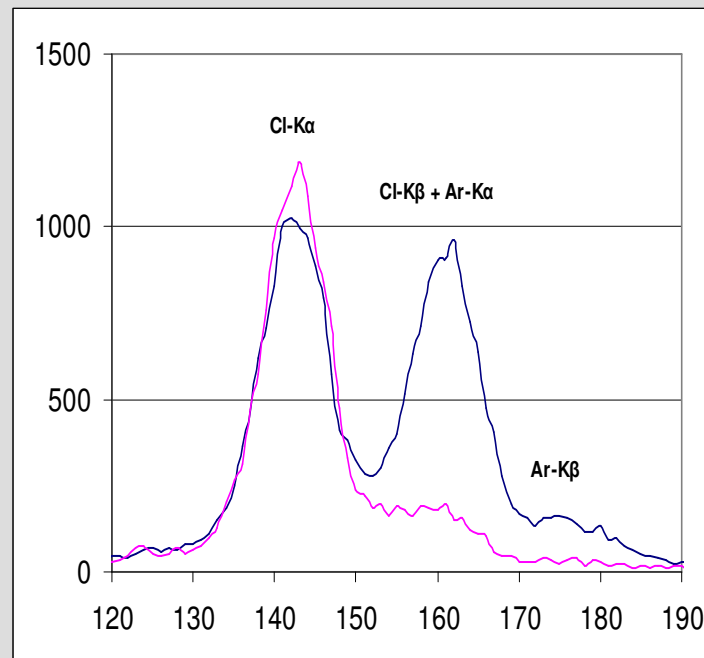


Experimental set-up

Wien Atom Institute TXRF module,
Fine Focus **Cu x-ray tube** (Seifert FK 60-04 AG)
High Voltage Generator (Seifert 150 Debyelex 3000) **30 kV** 20 mA
Oxford Si(Li) detector 80 mm² 155eV at 5.9 keV,
Irradiation Time =100 s, AXIL Integration Software

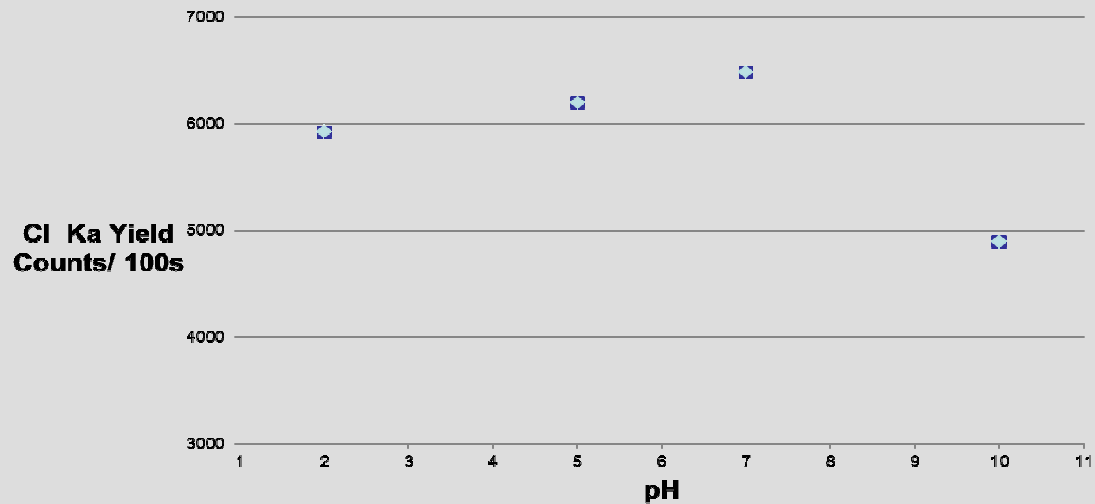


Spectra with (pink) and without (blue) Helium flux





pH effect



The results showed that analysis was independent of the pH of the solution in the range of **2 – 8**.

Changes are observed at higher pH values. At higher pH values the yield decreased due to the simultaneous response Perchlorate and hydroxide anions. The

Hydroxide ion compete with perchlorate ion for the cationic site in the membrane.

-At lower the membranes have poor response (decomposition, poor stability)



Chloride Removal

Drinking water spiked with perchlorate



Silver Nitrate addition



Stirring and heating until boiling for 30 min



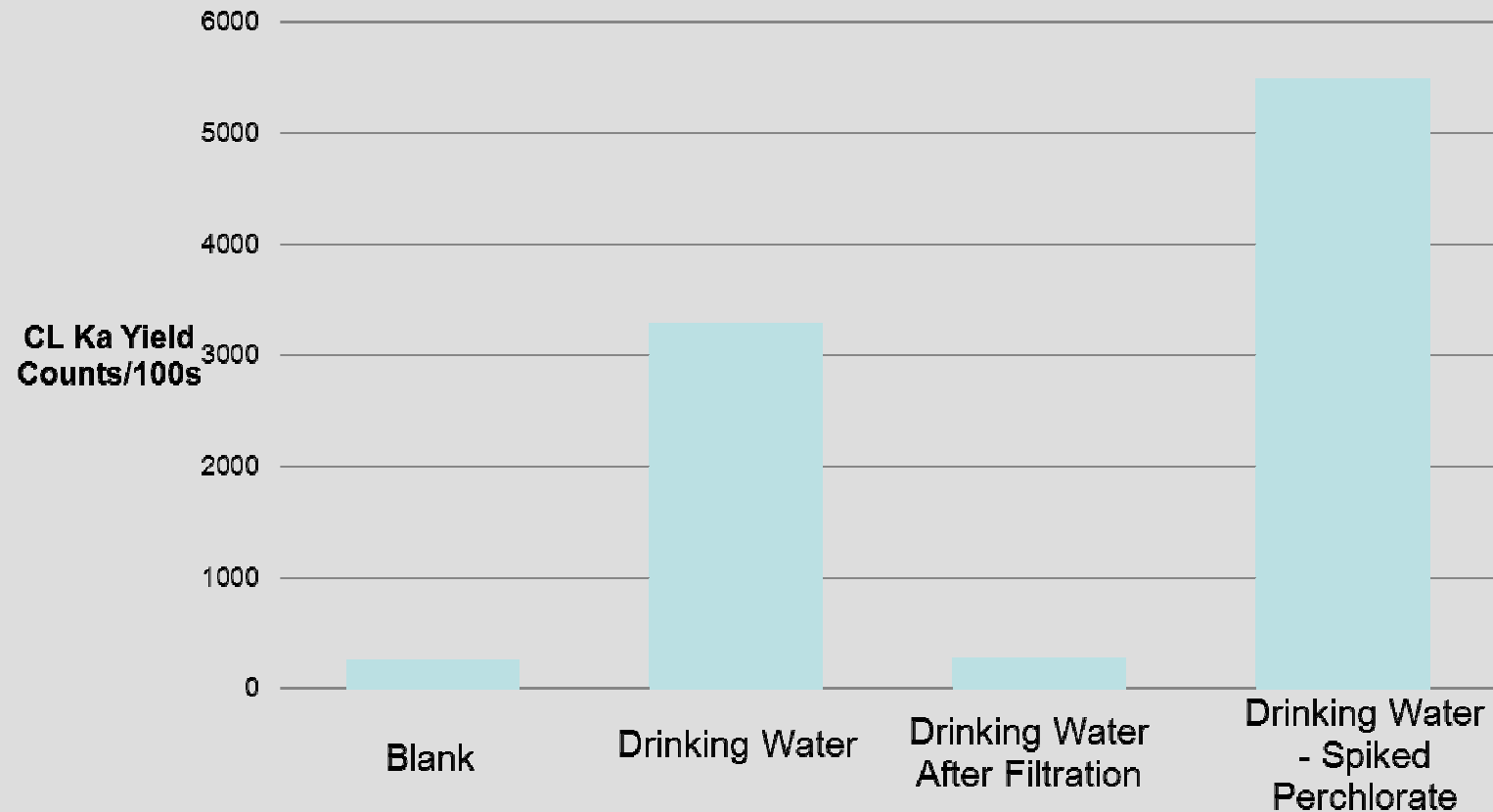
Production of white precipitate AgCl



Filtering with Buchner



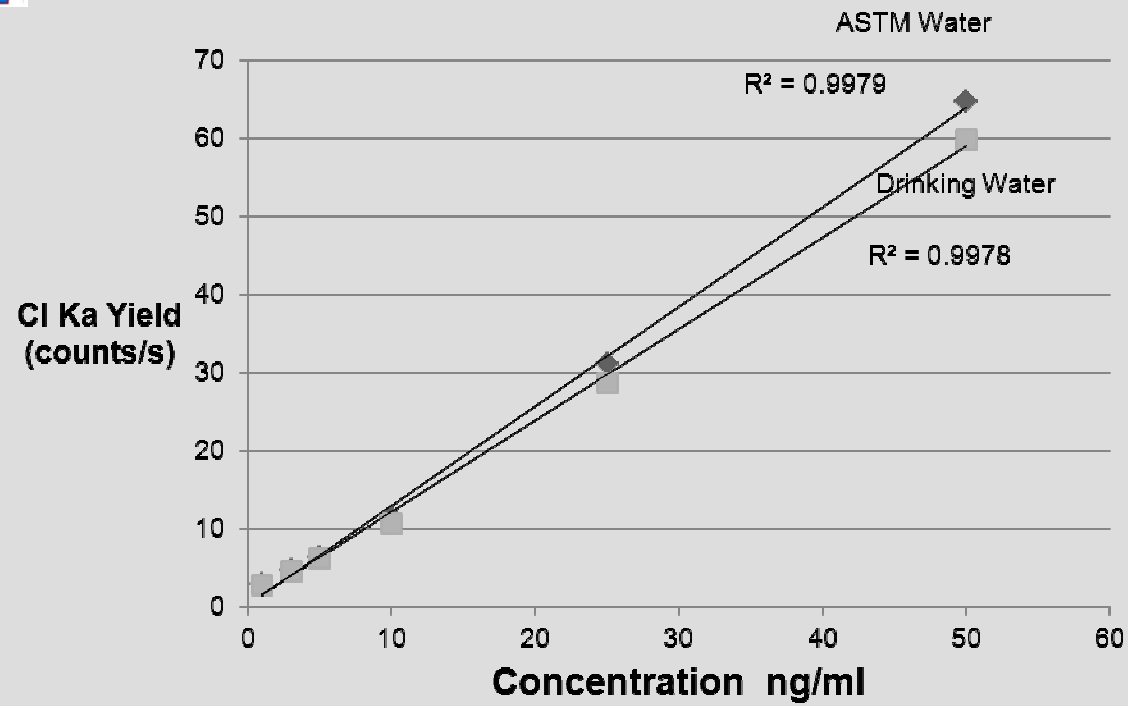
Chloride Removal



Blank = EVA membrane+Phenolphthaleine (no immersion) due to Aliquat ion exchanger

Drinking water => 11.7 ppm chloride

Drinking water Spiked perchlorate => 50 ng/mL (ppb) perchlorate spike⁵³



Drinking Water Minimum Detection Limit: 0.8ng/mL (100 s)



- ✓ The proposed liquid perchlorate selective membranes could be used for perchlorate analysis
- ✓ The best membrane was based on EVA + phenolphthaleine system
- ✓ Determination of perchlorate ions is possible in drinking/mineral water samples (after chloride precipitation).
- ✓ Chloride precipitation does not affect perchlorate
- ✓ There was good selectivity, long term stability and applicability over a wide pH range.
- ✓ Minimum detection limit = 0.8 ng/mL (ppb) for 100 s irradiation time. The MDL is suitable for environmental analyses as EPA Drinking Water Equivalent Level is 24.5 ppb
- ✓ Very good adhesion of the membrane
- ✓ Very low chemical reagent consumption



4) Membrane Analysis Applications

Cation Analysis

Mercury

Anion Analysis

Perchlorate

Bromate

Cation + Anion Analysis

Chromium



5) TXRF – Reagent Immobilization Analysis



Anion Analysis - Bromate

Anal. Chem. 2007, 79, 2827–2832

Bromate Determination in Water after Membrane Complexation and Total Reflection X-ray Fluorescence Analysis

Vasilios S. Hatzistavros, Pavlos E. Koulouridakis, Ioanna I. Aretaki, and Nikolaos G. Kallithrakas-Kontos*

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Drinking water ozonation – Bromide → Bromate (suspected human carcinogen)



Table 1. Membranes of Various Matrix Compositions That Were Tested for Bromate Selection Ability^a

no.	matrix	Plasticizer (dibutyl phthalate) %	aliquat-336 %	solvent
1	PVC (57%)	14	29	THF
2	CTA (57%)	14	29	CHCl ₃
3	CTA (28%)	62	10	CHCl ₃
4	EVA (60%)		40	CHCl ₃
5	PVC (40%)	50	10	THF
6	EVA (50%)		50	CHCl ₃
7	EVA (55%)		45	CHCl ₃
8	PVC (60%)	25	15	THF
9	PVC (50%)	25	25	THF
10	PVC (65%)	17.5	17.5	THF
11	CTA (50%)	25	25	CHCl ₃
12	PVC (60%)	20	20	THF
13	PVC (60%)	15	25	THF

^a PVC = poly(vinyl chloride), CTA = cellulose triacetate, EVA = poly(ethylene-*co*-vinylacetate), THF = tetrahydrofuran.

Complexing Reagent. The ligand solutions were prepared by the dissolution of 3 mg of complexing reagent to 2 mL of high-purity water. The tested ligands were the following: L1, *o*-dianisidin (Fluka Chemika no. 33430); L2, antipyrin (Aldrich 200-486-6); L3, 5-(4-dimethylamino) benylidene-rhodamine (Fluka Chemika no. 32020); L4, phenyl acetate (Aldrich 108723); L5, morin hydrate (Fluka Chemika 69870); L6, dithizone (Fluka Chemika no. 43820); L7, chlorpormazine (L 437905); L8, 1-nitroso-2-naphthol (Fluka Chemika 73910); L9, 4-nitrocatechol (Aldrich 17960); L10, thiourea (Riedel-de Haen no. 33717); L11, citric acid

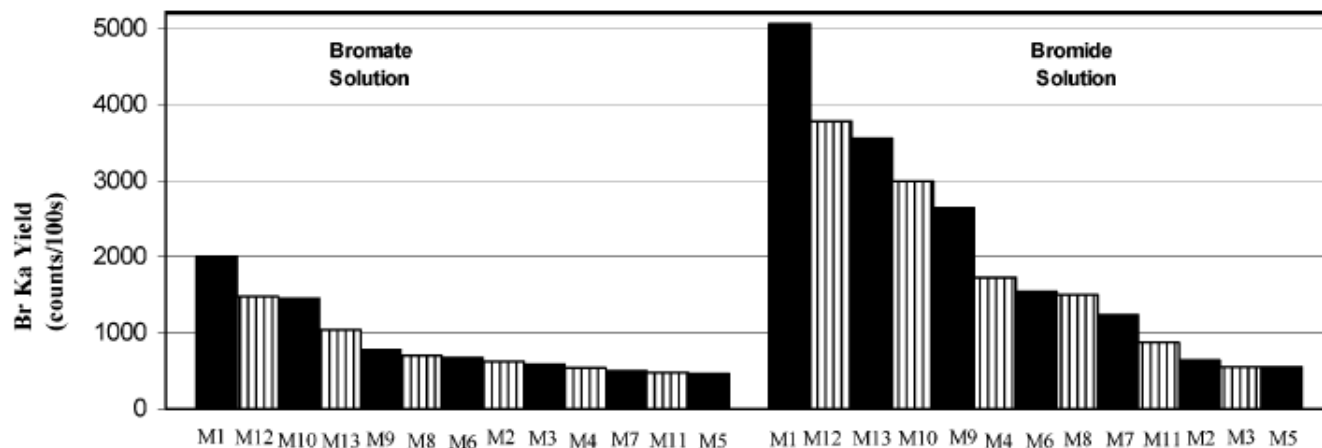


Figure 2. Comparison of various membrane matrixes toward bromate and bromide X-ray yield. The Br X-ray yield is obtained in separate bromate and bromide solutions without a complexing agent.

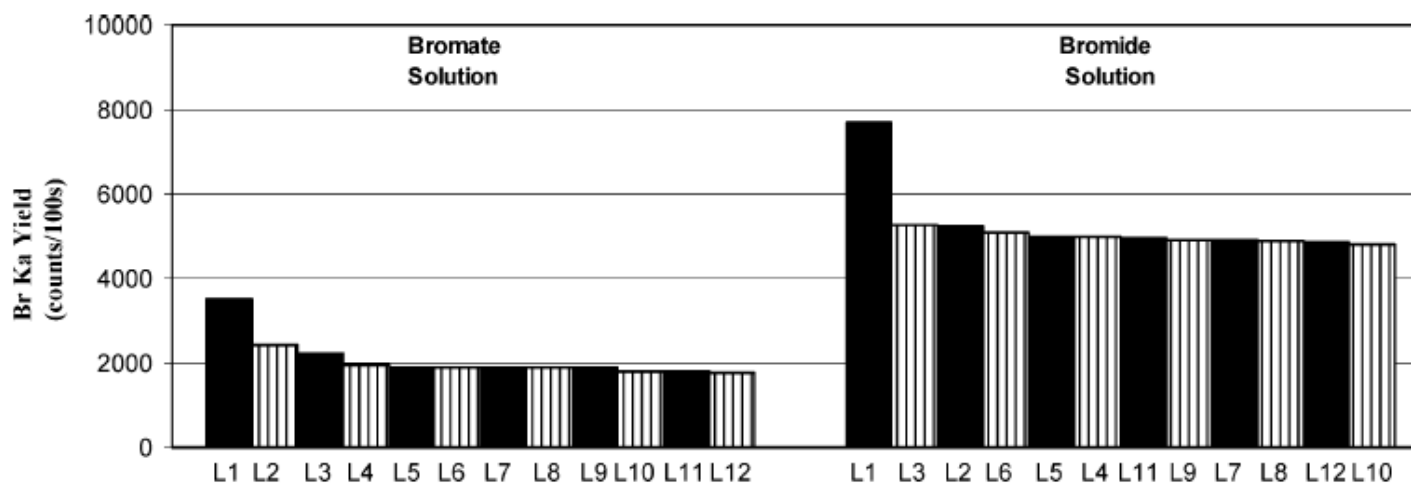


Figure 3. Comparison of 12 different complexing ligands for bromate and bromide complexation upon membrane M1. Enhancement of the Br X-ray yield compared to that of Figure 1 (only matrix) was observed. *o*-Dianisidin demonstrated the best yield among all the other complexing agents. The ligands used are mentioned in the Experimental Section.

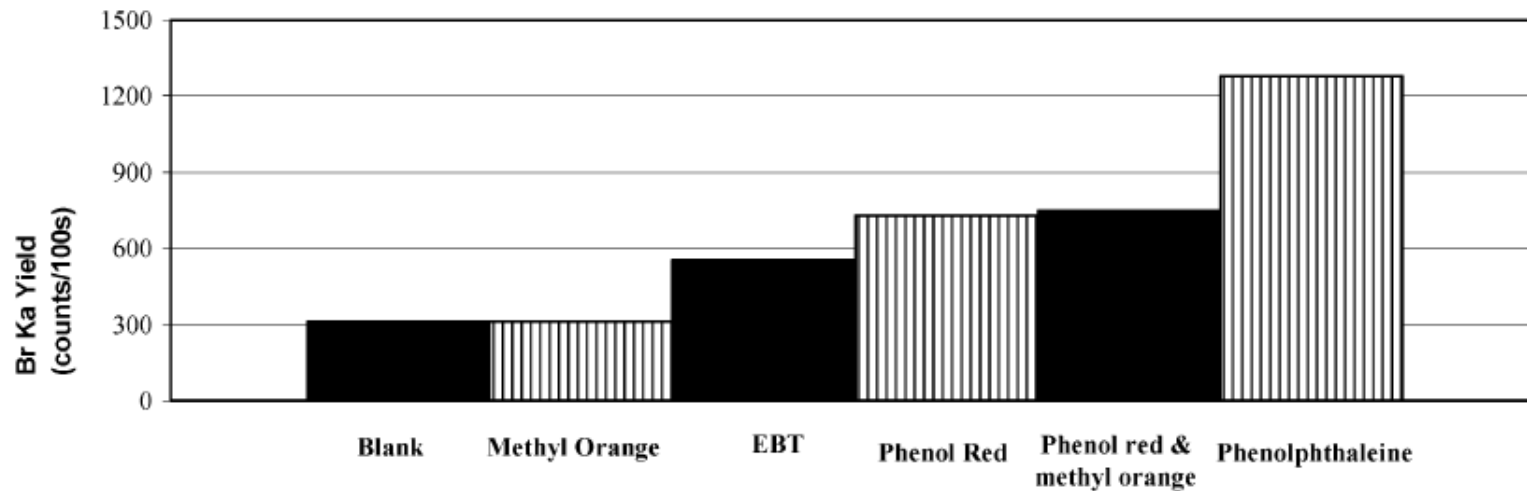
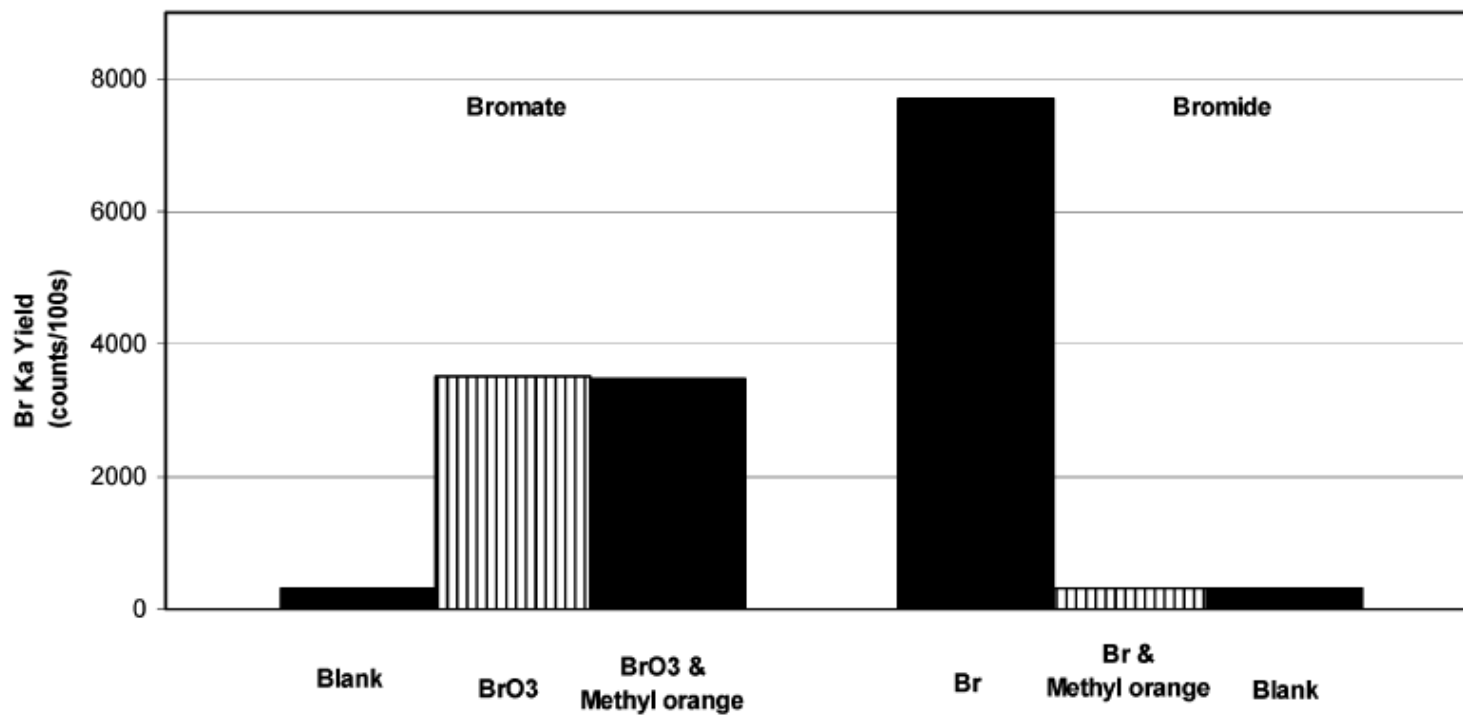


Figure 4. Bromide X-ray yield as a function of the presence of different masking agents in the sample solution; Br X-ray yields should be around 8000 counts/100 s if the masking agents were absent. The bromide concentration was 50 ng/mL, and the solution volume was 50 mL (no bromate ions were present).



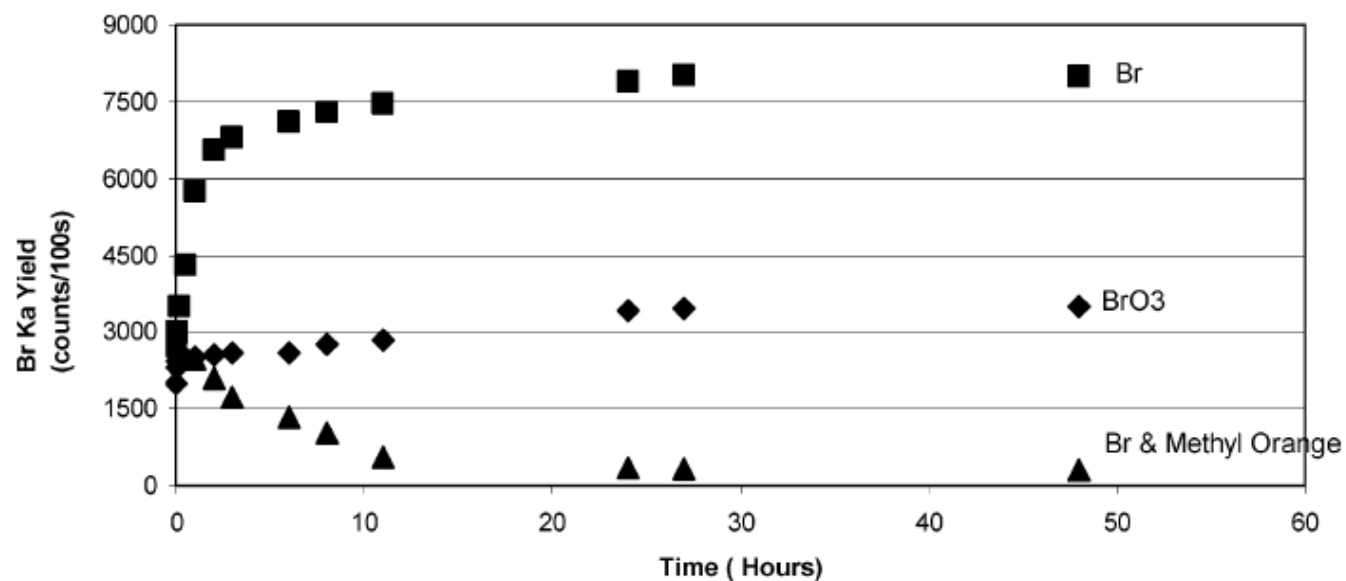


Figure 7. Bromine K α X-ray yield as a function of the membrane equilibration time in a 50 ng/mL solution. Bromate, bromide, as well as bromide with methyl orange solutions were analyzed.

Table 2. Bromate Yield as a Function of Different pH Values of the Analyzed Solutions (Bromate Concentration 10 ng/mL)

pH	bromate yield
2.0	7.94 ± 0.32
4.0	7.93 ± 0.34
6.0	7.94 ± 0.32
7.0	7.97 ± 0.34
8.0	7.94 ± 0.35



1. Bromate complexation was achieved with a PVC + aliquat-336 membrane using as the ligand *o*-dianisidin.
2. The use of the masking agent methyl orange led to the complexation of the bromide ions in the solution but not of the bromate ones, avoiding bromide interference.
3. The collection of bromate on the membrane took place in the first 10 h.
4. Good linearity existed for the 1–25 ng/mL bromate concentration range for both high-purity and drinking water.
5. The minimum detection limit was 1.0 ng/mL for drinking water and 0.9 ng/mL for the high-purity water.



Membrane Analysis Applications

Cation Analysis

Mercury

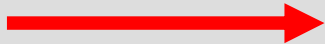
Anion Analysis

Perchlorate

Bromate

Cation + Anion Analysis

Chromium



TXRF – Reagent Immobilization Analysis



Cation + Anion Analysis

Chromium speciation

Research Article

X-RAY
Spectrometry

Received: 11 December 2007

Revised: 26 November 2008

Accepted: 29 November 2008

Published online in Wiley InterScience: 16 January 2009

(www.interscience.com) DOI 10.1002/xrs.1141

Chromium speciation by TXRF analysis

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Chromium (Cr) is an element which usually occurs in two different forms, Cr(III) and Cr(VI). As Cr(VI) is much more toxic than Cr(III), no complicated analytical methods with low detection limit are needed for chromium speciation. In the present work, a new method is presented for chromium speciation at low concentrations by selective membrane collection and total Reflection x-ray fluorescence (TXRF) analysis. Various membranes were produced on the surface of quartz reflectors containing different complexing ligands in Nafion and poly vinyl chloride (PVC) matrices. The membranes were produced on the surface of quartz glass, while the reflectors were immersed in water solutions with low concentrations of chromium salts for many hours. When the equilibration stage was achieved, the reflectors were analyzed by TXRF. Completely selective membranes for Cr(III) and Cr(VI) were prepared with minimum detection limits lower than 0.6 ng.ml^{-1} (ppb) in drinking water. Copyright © 2009 John Wiley & Sons, Ltd.



hexavalent chromium - K_2CrO_4 or $K_2Cr_2O_7$

Table 1. Components proportions of the produced membranes

Membrane name	Polymer type	Polymer (%)	Dibutyl phthalate plasticizer (%)	anion extractant Aliquat-336 (%)	Solvent
M1	PVC	57	14	29	THF
M2	CTA	57	14	29	CH ₃ Cl
M3	CTA	28	62	10	CH ₃ Cl
M4	EVA	60	–	40	CH ₃ Cl
M5	PVC	40	50	10	THF
M6	PVC	60	20	20	THF
M7	PVC	60	15	25	THF
M8	PVC	55	10	35	THF
M9	PVC	50	10	40	THF
M10	EVA	65	–	35	CH ₃ Cl
M11	EVA	55	–	45	CH ₃ Cl
M12	EVA	50	–	50	CH ₃ Cl

PVC: Poly vinyl chloride

CTA: cellulose-triacetate

EVA: polyethylene-co-vinyl acetate

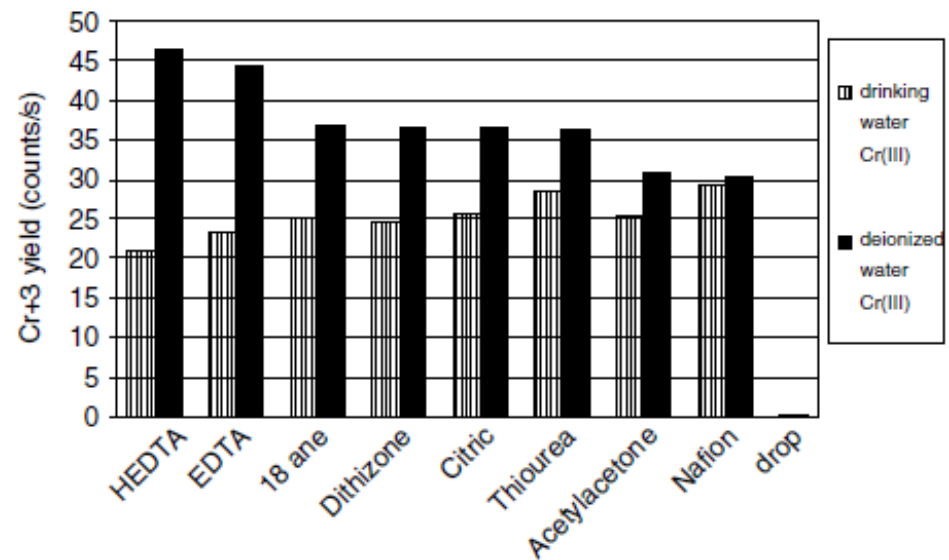


Figure 1. Comparison of various membrane ligands toward chromium Ka x-ray yield. The Cr x-ray yield is obtained in 50 ppb chromium (III) solution.

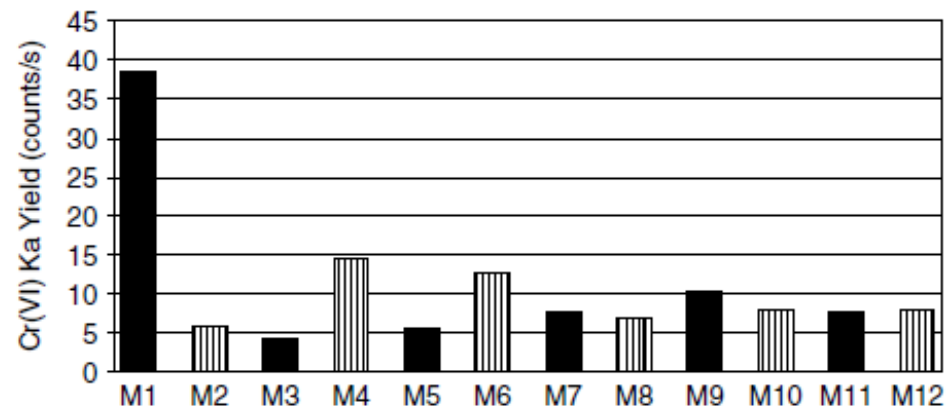


Figure 2. Comparison of various membranes Cr(VI) Ka yield.

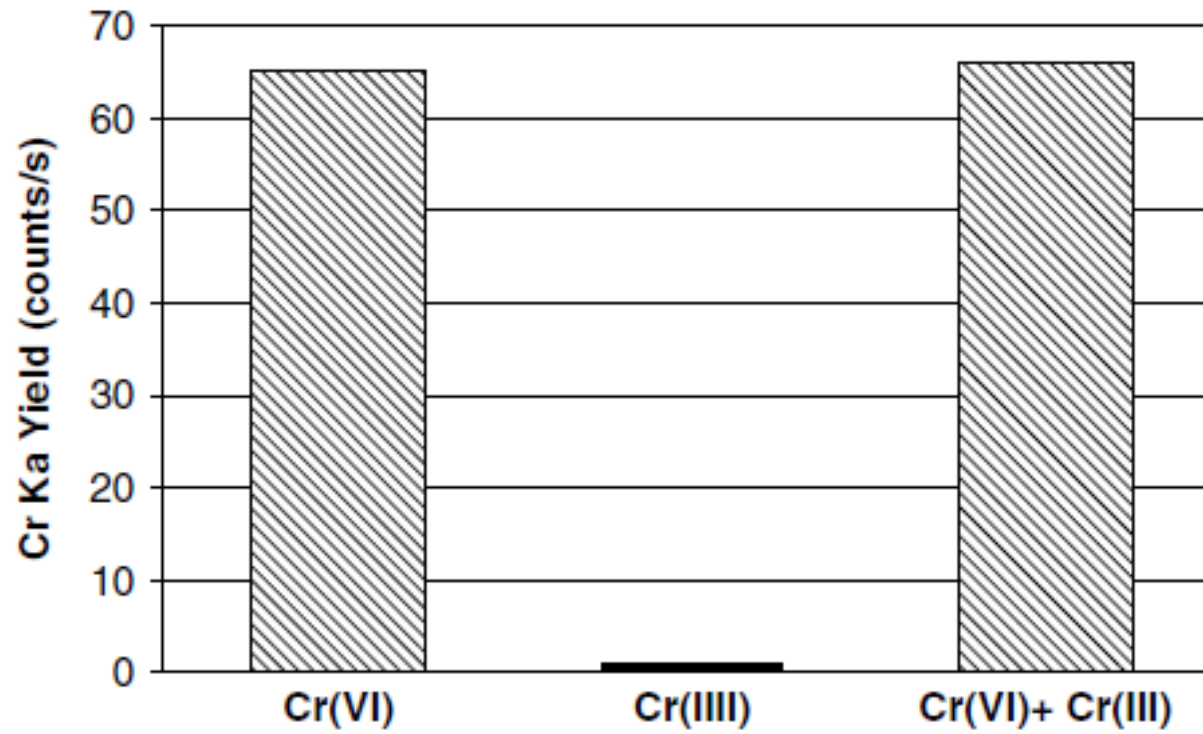
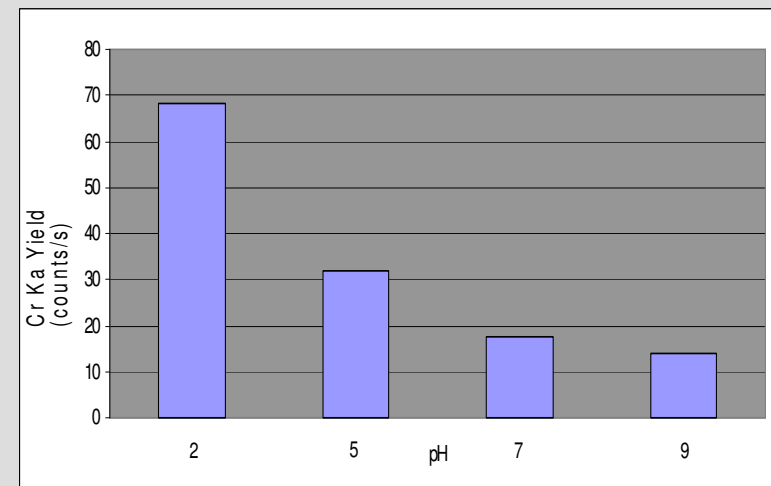
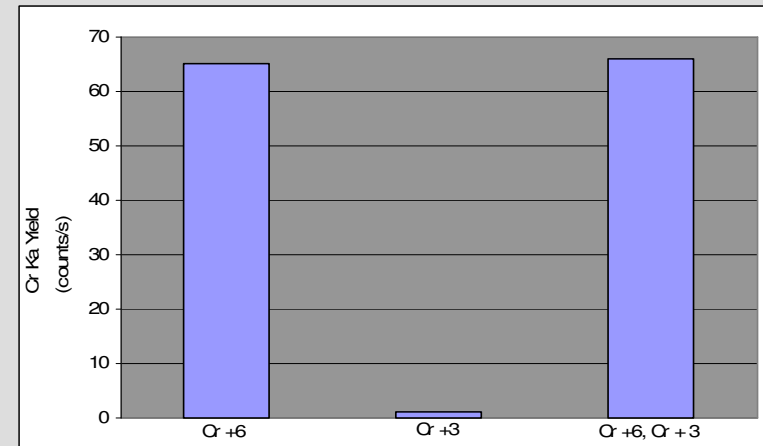


Figure 4. Membranes selectivity towards Cr(VI) and Cr(III) ions.



Cr(VI) Speciation

- PVC based membrane selective towards Cr(VI)
- anions and not to Cr³⁺
- Low detection limits 0.6 ppb
- Cr(VI)
- is Known to cause health problems when inhaled, or skin contact or drinking like cancer, respirator problems, skin rushes contrary to Cr³⁺
- Acidic conditions required (pH = 2) for the best detection of Cr(VI)
- Very good linearity in a wide range of concentrations of Cr(VI)
- in high purity and drinking water





4) Membrane Analysis Applications

Cation Analysis

Mercury

Anion Analysis

Perchlorate

Bromate

Cation + Anion Analysis

Chromium



5) TXRF – Reagent Immobilization Analysis



TXRF – Reagent Immobilization Analysis



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Analytica Chimica Acta 562 (2006) 252–257

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Total reflection X-ray fluorescence mercury analysis after immobilization on quartz surfaces

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Received 15 November 2005; received in revised form 24 January 2006; accepted 25 January 2006

Available online 2 March 2006

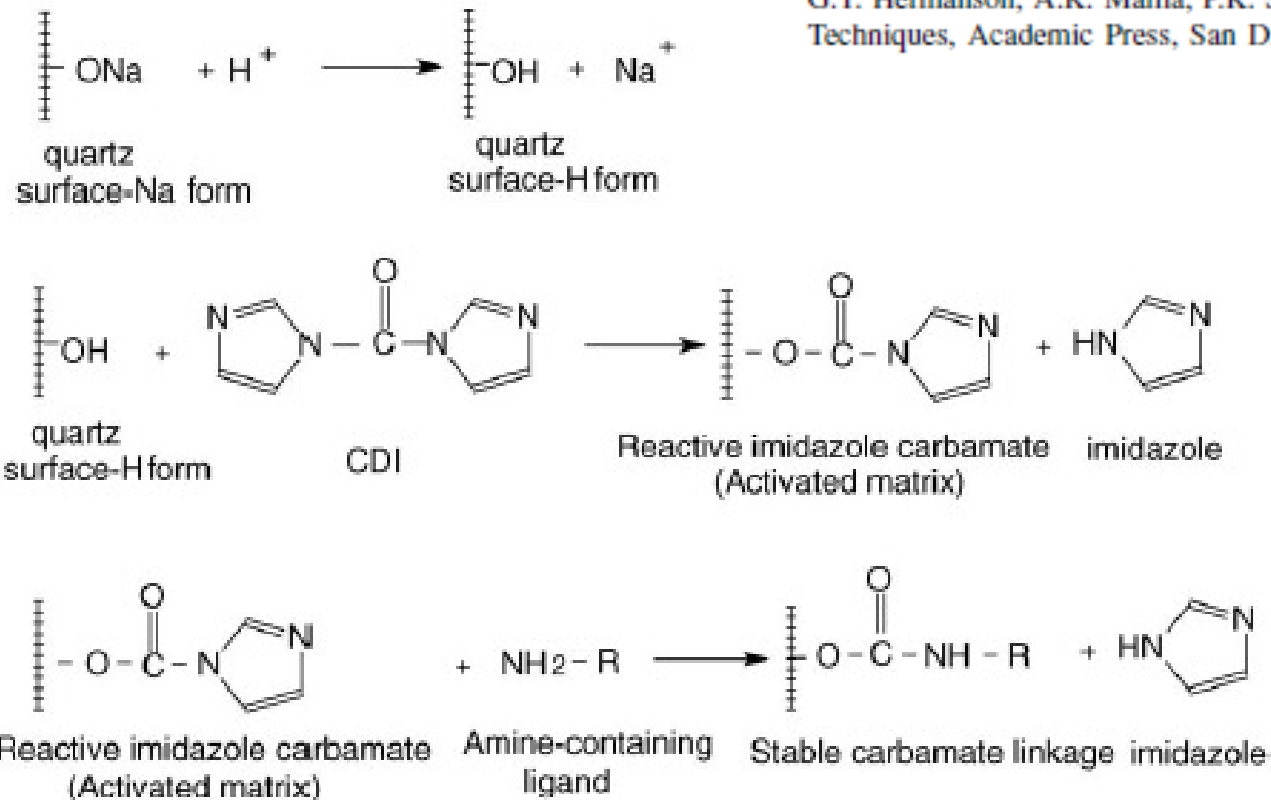
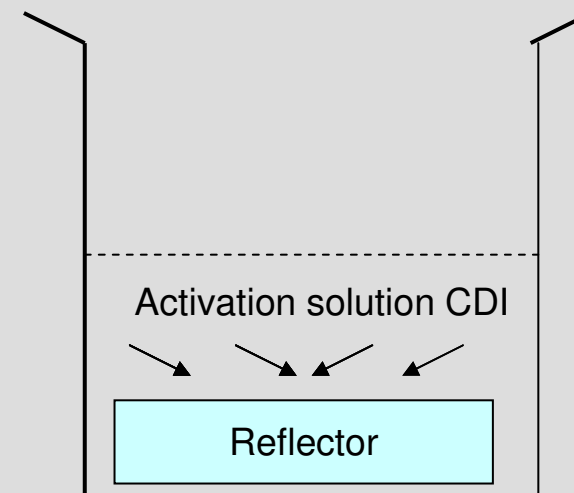


Fig. 1. The chemical reactions that took place during immobilizing procedure.

Activation with 1,1-carbonyldiimidazole (CDI) is a rapid method (75 min are enough). CDI is a highly reactive carbonylating reagent suitable to activate carboxyl or **hydroxyl** groups before the immobilization of amine-containing ligands. CDI is efficient, cheap and it is no pH dependent. The linkage of the amino group of the ligand to the support (Nalkylcarbamate) was shown to give good stability. The support has an excellent withstand to hydrolysis. Other advantages of CDI activation are the ability to achieve a range of substitutions under different conditions and the neutral carbamate linkage between the support and the ligand. The lack of a charge in the ligand linkage is important for the maintenance of specificity and for the reduction of the non-specific adsorption⁷¹ effects. An additional advantage is that CDI allows reproducible results.



Quartz Activation procedure



Quartz reflectors (two at each beaker 100 mL) were immersed in 30mL of HCl 0.05M for 1 h at room temperature. The objective was to replace sodium ions with hydrogen from the surface of the reflector. After 1 h, the reflectors were washed sequentially with water, then with solutions of 30% acetone/70% water, 70% acetone/30% water, and finally, with 100% acetone. The reflectors must not be dried between the acetone washes. The CDI activation solution was prepared by dissolving 0.5 g CDI in 20mL of acetone. The reflectors were immersed in the solution and the activation procedure was carried out under stirring at room temperature for 75 min. The activated reflectors were washed with acetone to remove the free imidazole, generated during the activation. The reflectors can be stored in dry acetone at 4 °C or used immediately. The beakers that were used in this process were made from glass.



Ligand immobilization procedure

Table 1
Complexing reagents examined for mercury collection

No.	Reagent	No.	Reagent
1	4-(2-Pyridylazo-resorcinol)	7	Antipyrine
2	4-Dimethylaminobenzal-rhodanine	8	4-Aminosalicylic acid
3	4-Nitrocatechol	9	Thiourea
4	<i>o</i> -Dianisidine	10	Citric acid
5	Dithizone	11	HEDTA
6	4-Methyl catechol	12	Blank

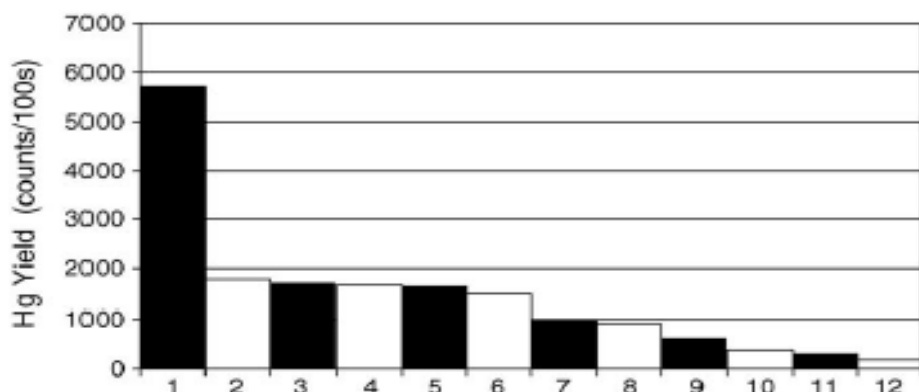
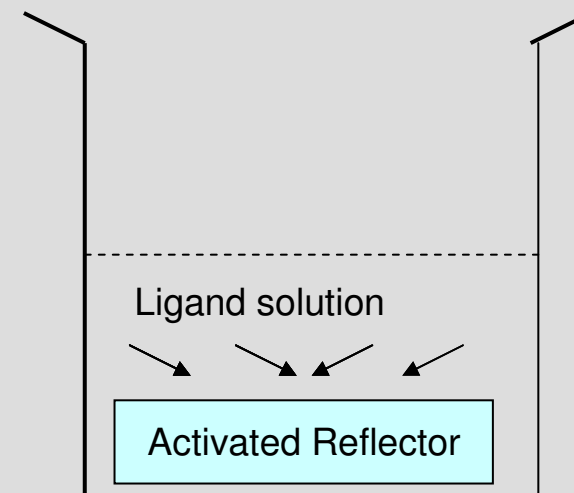


Fig. 2. Mercury L α X-ray yields as a function of the immobilized ligand. The names of the used reagents are given in Table 1. The mercury concentration was equal to 500 ng mL $^{-1}$ and the solution volume was 30 mL.



The activated reflectors were treated with 20mL of ligand solution at 4 °C for 20 h. Then the reflectors were extensively washed with acetone to remove any unreacted ligand and are left to dry for few minutes.

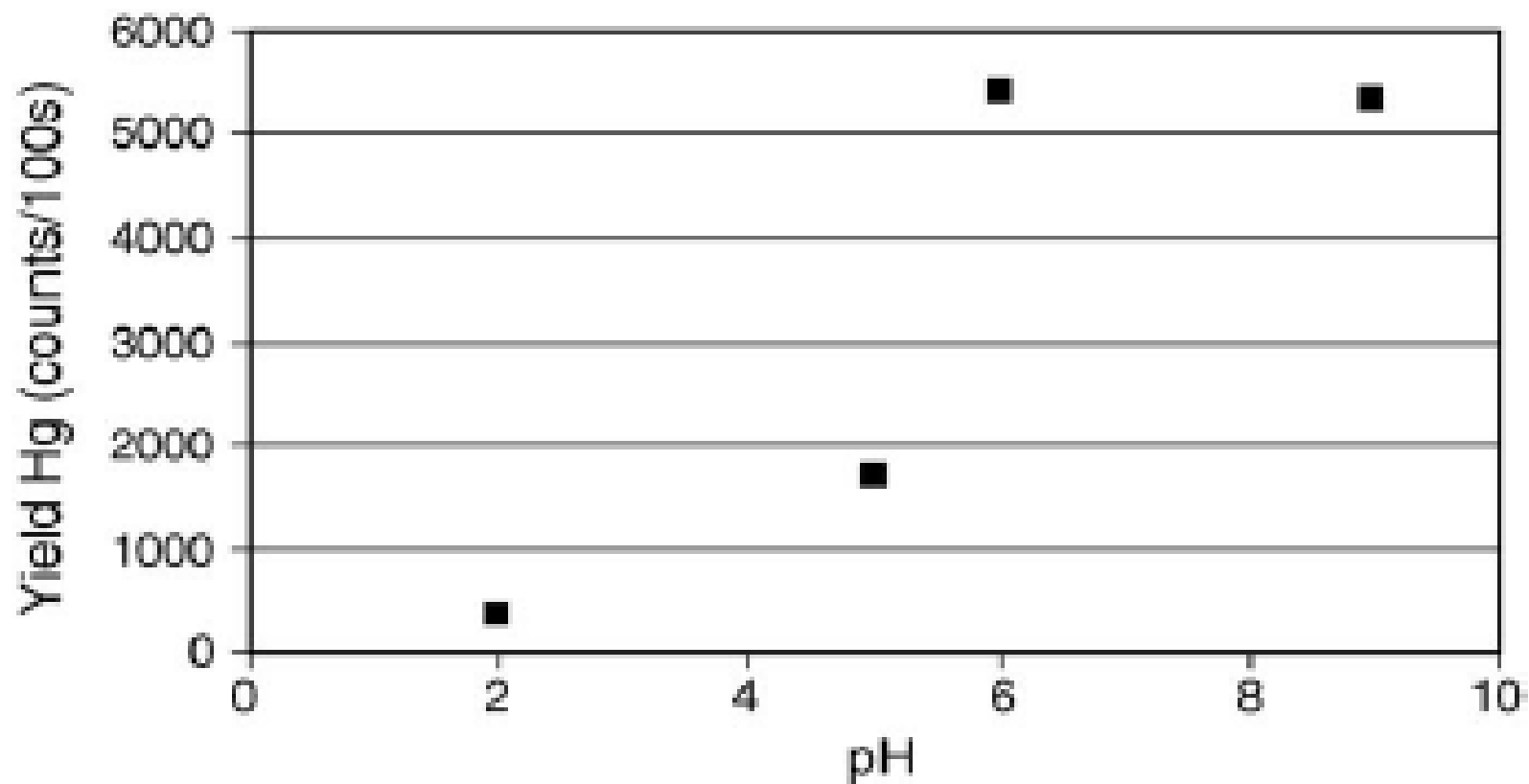


Fig. 4. The effect of pH on mercury $L\alpha$ X-ray yields (Hg concentration 500 ng mL^{-1} , equilibration time 10 min).

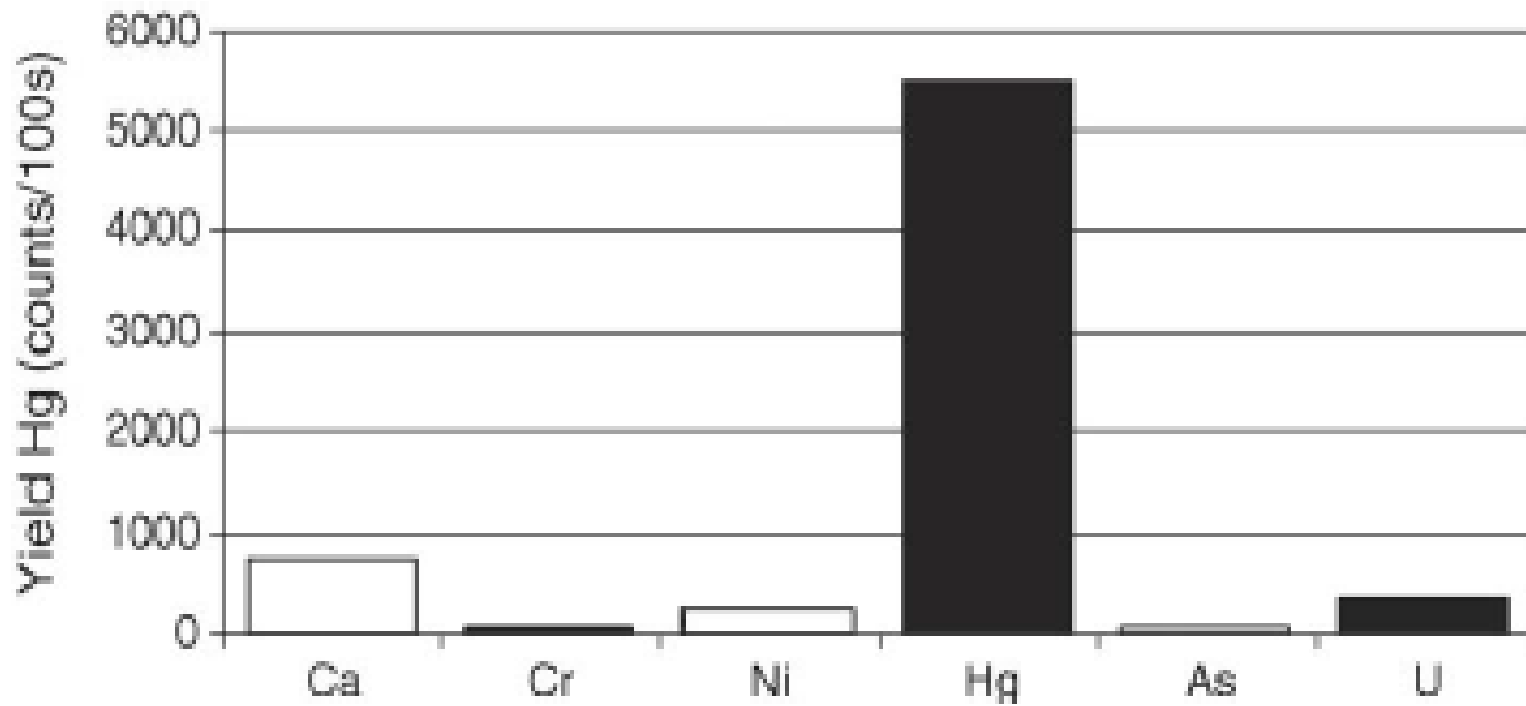


Fig. 5. Selectivity of the method compared to other ions (concentration equal to 500 ng mL^{-1} for all ions, equilibration time 10 min).

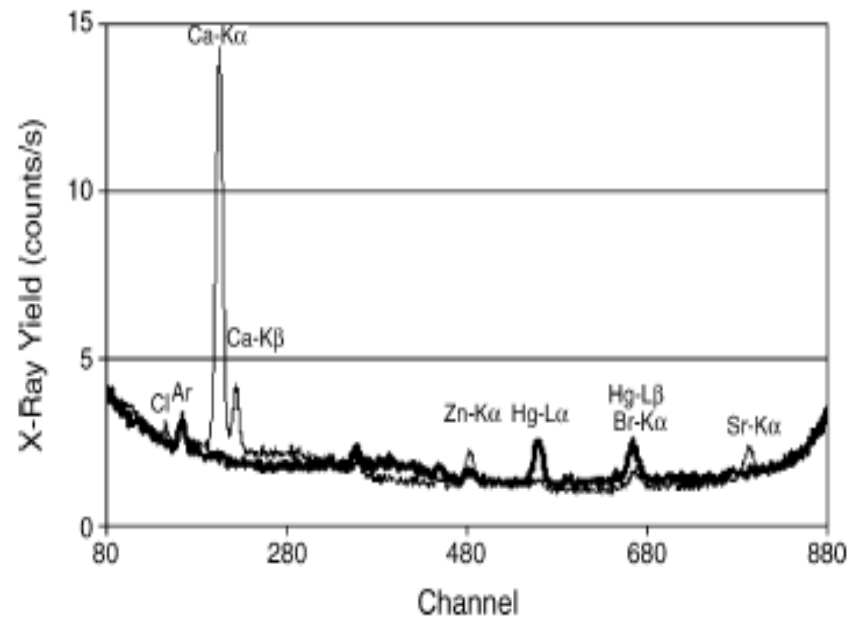


Fig. 7. Comparison of the mercury X-ray peaks which were collected with two different procedures. In the light line spectrum, 10 μL of 100 ng mL^{-1} mercury spiked drinking water had been dried on a quartz reflector (usual procedure). In the bold line spectrum, the same water solution was analysed according to the new procedure (CDI, 4-(2-pyridylazo-resorcinol) immobilization) introduced in



- It was possible to immobilize mercury ions on quartz reflectors and to analyse them directly by TXRF.
- CDI quartz activation with 4-(2-pyridylazo-resorcinol) immobilization gave the best results among all ligands.
- Seventy-five minutes CDI activation and 20 h complexing reagent immobilization time were satisfactory.
- Good equilibration time for the analysed samples were 4–15 min.
- Mercury speciation was achieved; methyl mercury was not selected.
- Very good selectivity of mercury compared to many other ions was observed.
- Very good linearity in the 1–500 ng mL⁻¹ mercury concentration range for both pure and distilled water existed.
- The minimum detection limits of mercury in distilled and drinking water were 2.5 and 5 ng mL⁻¹, respectively, for 900 s irradiation time.



The list of the TXRF analysed ions with their Minimum Detection Limits in drinking water and the best membrane composition (300 s irradiation time).

Analysed ion	MDL (ppb)	Membrane Composition / Method
Cr⁺³	0.2	Nafion [®] + HEDTA(N-(2-Hydroxyethyl)-ethilenediamine-N,N',N'-triacetic acid) / TXRF
Cr(VI)	0.4	PVC + Dibutyl Phthalate + Aliquat336 / TXRF
BrO₃⁻	2	PVC + Aliquat336 + o-Dianicidin / masking agent: Methyl orange / TXRF
ClO₄⁻	0.5	EVA + Aliquat336 + Phenolophtaleine / Cl ⁻ removal / TXRF
Hg⁺²	0.2	PVC + Dibutyl phthalate + 5,5'-Dithiobis(2-nitrobenzoic acid) + Dithizone / TXRF
Hg⁺²	0.1	PVC + Dibutyl phthalate + 5,5'-Dithiobis(2-nitrobenzoic acid) + Dithizone /on thin Mylar/1000 mL analysed solution/ EDXRF
		Reflector Activation / Reagent Immobilization
Hg⁺²	9	Reflector Activation CDI, Reagent Immobilization 4(2- pyridylazo)resorcinol / TXRF