PROJECT REPORT
13 - 00

Rannsóknastofnun fiskiðnaðarins

JUNE 2000

APPLICATION OF BLOODHOUND BETA- INSTRUMENTS (BH213) FOR FISH PRODUCTS

PROFILE - QD, CT98 - 3436

Guðrún Ólafsdóttir

Skýrsluágrip Rannsóknastofnunar fiskiðnaðarins

Icelandic Fisheries Laboratories Report Summary

Titill / Title	Application of Bloodhound Beta-Instruments (BH 213) for Fish and Fish Products		
Höfundar / Authors	*Guðrún Ólafsdóttir*		
Skýrsla Rf /IFL report	13	*Útgáfudagur / Date:*	June 2000
Verknr. / project no.	1382	PROFILE - QD, CT98-3436	
Styrktaraðilar / funding:	European Commission		
Ágrip á íslensku:	Skýrslan er framlag Rf í Evrópuverkefnið PROFILE-QD (Rafræn greining á lykt matvæla og drykkja í gæðamati). Gerðar voru samanburðartilraunir til að meta hæfni rafnefs, sem byggir á "Discotic Liquid Crystal" (DLC) tækni, til að meta ferskleika og gæði fiskafurða og gefa hugmyndir um úrbætur. Hlutverk Rf var jafnframt að meta gagnsemi tækninnar fyrir fiskiðnað og kynna niðurstöður tilrauna á fundum og á ráðstefnum. Á fyrsta ári verkefnisins var lögð áhersla á að safna upplýsingum um rokgjörn efni í fiski sem eru mikilvæg til að fylgjast með ferskleika og skemmd. Á öðru ári voru prófaðar tvær frumgerðir af tækinu við mælingar á fiskafurðum af mismunandi gæðum ásamt mælingum á stöðlum. Erfiðleikar við þróun og framleiðslu á DLC skynjurum hafa valdið töfum í verkefninu. Auk þess reyndust skynjararnir ekki eins vel og til stóð. Prófanir á frumgerðunum sýndu að endurtekningarhæfni og næmni var ábótavant, auk þess sem mengun skynjaranna olli vandræðum. Skynjararnir voru lengi að ná sér eftir mælingar á sýnum með háan styrk af rokjörnum efnum. Þessi vandkvæði hamla notkun tækisins og úrbóta er þörf áður en þessi tækni mun nýtast í rafnef.		
Lykilorð á íslensku:	*rafnef, disklaga vökvakristallar, ferskleika og gæðamælingar*		

Skýrsluágrip Rannsóknastofnunar fiskiðnaðarins

Icelandic Fisheries Laboratories Report Summary

Summary in English:	This report summarizes the contribution of IFL to the EU project PROFILE-QD (Electronic Profiling of Food and Beverage Odour for Quality Determination, CT98-3436). Comparative studies were done to evaluate the performance of a Discotic Liquid Crystal (DLC) based instrument for fish and fish products and provide feedback on the effectiveness of the new instrument to detect the freshness of fish products. The role of IFL was also to validate the technology in terms of usefulness in the fish industry and disseminate results from the testing at meetings and conferences. During the first year of the project the focus was on collecting information about volatile compounds in fish that are important to monitor fish freshness and spoilage. During the second year of the project the testing of different prototypes of the instrument was done. Delays in the delivery and poor performance of the DLC beta-instrument has been a major concern throughout the project time. Testing of the prototypes showed that reproducibility of measurements was poor and poisoning of the sensors was a major problem in addition to lack of sensitivity of the technique. The slow recovery of sensors after having been exposed to high concentration of standard compounds or samples with high levels of volatiles is troublesome and limits the use of the instruments. Further development is needed before the DLC technique can be applied in an electronic nose.
English keywords:	electronic nose, Discotic Liquid Crystals, freshness and quality measurements

Application of
Bloodhound Beta-Instruments (BH 213)
for Fish Products

Electronic Profiling of Food and Beverage Odour for Quality Determination
PROFILE - QD CT98-3436
Demonstration project

Final report March 1998 - June 2000

Partner 4 Icelandic Fisheries Laboratories
Gudrun Ólafsdóttir, gudrun@rfisk.is
Skulagata 4, 101 Reykjavik, Iceland
Tel.:+354 5620240, Fax:+354 5620740

Table of contents

I. Initial performance report - 1st year, 1998 - 1999

Analysis of volatile compounds in fish using electronic nose techniques

Introduction

The main objective of this demonstration project is to manufacture and demonstrate a sensor array system for use in the food and drinks industry which overcomes the problems of water vapour interference, irreproducibility and lack of discrimination to volatile food components. In addition some progress towards tuned selectivity and relative quantitation will be addressed. The role of IFL in the project was to carry out comparative study of the performance of a DLC based instrument for fish and fish products and provide feedback on the effectiveness of the new instrument to detect the freshness of fish products. Also to validate the technology in terms of usefulness in the fish industry. IFL participated in Sub Task 7.1 Internal placement and validation and Sub Task 7.2 Demonstration Platform Meeting.

The activities during the first year of the project have mainly been focused on 1) identification of volatiles in fish to enable systematic construction of sensor arrays for fish application and 2) standard testing of samples with comparative techniques to identify the best sampling procedures for volatile profiling.

To prepare for sub-task 7.1 and 7.2 the following has been done at IFL:

i) Information collected about volatile compounds in fish that are important to monitor fish freshness and spoilage.

ii) Sampling - suggestions how to evalute the performance of the instrument, reproducibility, sampling optimisation and calibration.

iii) Preparation for Demonstration Consortium Meeting and other dissemination activities.

i) Volatile compounds in fish

The volatile compounds that contribute to fresh and spoiled odours of fish are well known. The main classes of compounds that are present in fish and contribute to fresh odours are alcohols and carbonyls (C6-C9) but these compounds are present in very low concentrations (ppb) and their detection may therefore be difficult using electronic noses. However, the compounds that contribute to spoilage odours, are present in much higher concentration and can be expected to be detected by electronic nose. These are volatile, degradation compounds that are microbially formed during spoilage of fish. The formation of short chain alcohols, ketones, aldehydes, amines, sulphur compounds, aromatics and acids occurs as a result of microbial degradation of amino- and fatty acids. The concentration of these microbially formed compounds increases with time as the fish spoils and some of them have been used as indicators of spoilage.

Ammonia, trimethylamine (TMA), ethanol, hydrogen sulphide, methyl mercaptan and sulphides are typical spoilage compounds that exhibit odours such as fishy, stale, rotten and putrid and are present in the headspace above fish during spoilage at the parts per million level. Table 1 from the paper of Olafsdottir and Fleurence (1998) lists the main classes of compounds that are present in fish and contribute to the characteristic odour of fish.

Table 1. Classes of odours in fish and examples of compounds contributing to the odour.

Fish odour	Class of chemical species	Examples of compounds	Aroma description	Odour threshold in water
SPECIES	C6-C9 alcohols	Hexanal / t-2-hexenal,	Green, aldehyde-like	4,5ppb / 17ppb [37]
RELATED	and carbonyls	1-octen-3-ol, /1-octen-3-one	Mushroom	10ppb/ 0,009ppb[37]
FRESH		1,5-octadiene-3-ol	Heavy earthy, mushrooms	10ppb[37]
FISH		1,5-octadiene-3-one	Geranium	0,001ppb[37]
ODOUR		2,6-nonadienal	Cucumber	0,001ppb[37]
		3,6-nonadienol	Cucumber, melon-like	10ppb[37]
	Bromophenols	2,6-dibromophenol	iodine- and shrimp-like	0,0005µg/kg[22]
		2,4,6-tribromophenol	saltwater fish, brine-like.	0,6µg/kg[22]
		2-bromophenol	Sea, marine-like flavour	
	N-cyclic	Pyrrolidine	Earthy	
	compounds	piperidine		
	Short chain	ethanol, propanol, butanol,	solvent like	1-100 ppm[5]
	alcohols	3-methyl-1-butanol		
MICROBIAL	Short chain	acetone, butanone	solvent like	
SPOILAGE	carbonyls	ethanal, propanal		
ODOUR		3-methylbutanal	malty	0,06ppm [44]
		2-methylbutanal	malty	0,04ppm [44]
	Amines	ammonia,	ammoniacal	110 ppm[5]
		TMA	fishy, ammoniacal	30 ppm[5]
		DMA		0,6 ppm[5]
		histamine,		
		putrecine,	putrid, rotten	
		cadeverine		
	Sulphur			
	compounds	hydrogen sulphide	sulphury, boiled eggs	5-40 ppb [38]
		methylmercaptan	rotten, cabbage	0,05 ppb [38]
		methyl sulphide	cabbage-like	0,9µg/kg[39]
		dimethyl disulphide	putrid, onion-like	12 ppb [40]
		dimethyl trisulphide	putrid, cabbage and onion-	0.01ppb[40]
		bis-methylthio methane	garlic like	0,3 µg/kg[39]
		thioesters		
	Aromatics	phenethyl alcohol	old roses	2 ppm
		phenol,	phenolic,	300 µg/kg[39]
		p-cresol	pigpen-odours , horse manure	
	N-cyclic	indole	moth ball or faecal like	
	compounds	skatole		
		acetic acid,		34,2ppm[5]
	Acids	butyric acid	Sour, rotten, old socks	32,8ppm[5]
		isobutyric acid		
OXIDIZED	Unsaturated	hexanal	green, planty	4,5ppb[39]
ODOUR	aldehydes	c4-heptenal	cardboard-like, potato-like	0,04ppb[41]
		2,4-heptadienal,	fishy oxidised flavour	
		2,4,7-decatrienal,	burnt, fishy, cod-liver oil-like	
		2,4-heptadienal and	ripened anchovies	
PROCESSING		3,5-octadien-2-one		
ODOURS		methional	boiled potato - like odour	
		2-methyl-3-furanthiol	meaty odour in canned tuna	
ENVIRONMENTAL		methyl sulphide	petroleum odours	
ODOURS		geosmin		
		2-methyl-iso-borneol	earthy, muddy odours	

From: Olafsdóttir and Fleurence (1998)

ii) Sampling

To optimise and study the effect of different sampling conditions on the response of gas sensors instruments, experiments have been done at IFL with a different type of gas sensor instrument (FreshSense, Bodvaki (Element), Iceland) equipped with electrochemical gas sensors and a static headspace sampling system. IFL has been involved in research using the FreshSense instrument for several years (2-6). Based on experience of sampling techniques used for analysis of volatile compounds with gas chromotography techniques (7) it was decided to minimize sample preparation to make the measurement with an electronic nose more attractive for industry use as a rapid technique.

This work is part of the masters thesis of Aslaug Högnadottir in Food Science at the University of Iceland and was presented at the WEFTA (Western European Fish Technologists Association) meeting in Tromsö, Norway, 1998 (8). Similar experiments are planned to evaluate the performance of the DLC based instrument and the idea is to publish the results in a scientific journal (i.e. Sensors and Actuators). Principal component analysis (PCA) using the software Unscrambler (CAMO AS) was used to demonstrate that the FreshSense instrument could discriminate between samples.

Shrimp experiments - the effect of sample size and handling

The aim of this series was to evaluate the effect of sample size and sample handling on the response of the FreshSense instrument. Three sample sizes of shrimp were measured: 100, 500 and 1000 g and two different methods of thawing were evaluated. Firstly the shrimp was kept in sealed bag at 0°C overnight and warmed to 12°C at room temperature, and secondly the shrimp was kept in sealed in bag and warmed to 15°C in 38°C water.

The effect of mincing the sample in food processor was also evaluated.

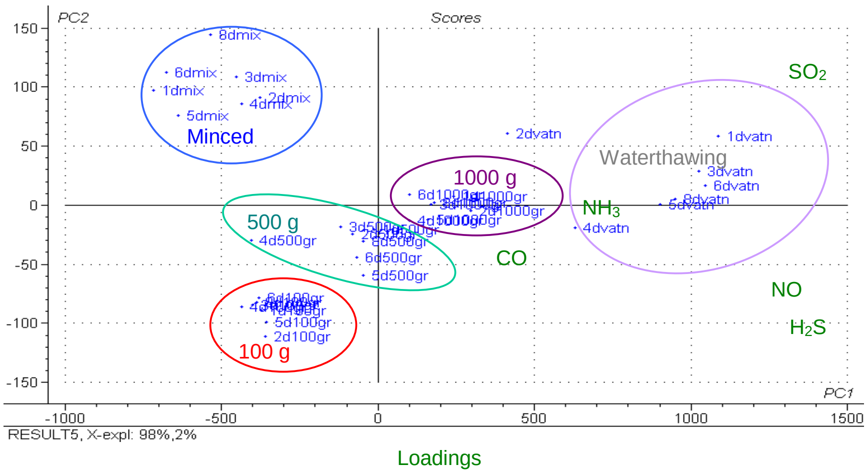


Figure 1. PCA biplot of FreshSense measurements of various sample sizes and sample preparation methods for shrimp. (From the Masters Thesis of Aslaug Högnadóttir, 1999)

Figure 1 shows that discrimination between different weight and handling of samples is good in the electronic nose. Sample size affects response, which increases with increasing sample weight. Using a mixer to homogenize samples results in lower sensor response. This may partly be because of less surface area because of much more dense matrix when homogenizing the sample. Thawing in water is rapid, but water temperature and time have to be monitored carefully and can be tedious in routine analysis.

Fishmeal - effect of sample size (weight and surface area)

A few samples of the same fishmeal batch were measured in duplicate to evaluate the effect of sample weight and temperature on the response of the sensors when surface area is the same. Sample size has some effect on response in particular if surface area is not the same. The surface area of 200 g sample and 600 g sample in the sample container was the same and therefore the difference in sensor response is negligible. The 50 g sample did not cover the same surface area and therefore shows slightly lower responses.

The results of these studies using shrimp and fishmeal showed that discrimination between different weight and handling of samples is achieved in the electronic nose. As expected sample size affects response and it increases with increasing sample size and the surface area of samples is very critical. The temperature during sampling is also very important and it is evident that temperature affects the sensor´s responses, depending on the identity and characteristics of volatiles in the sample. The effect of temperature is very crititcal and has to be optimised for each sample and monitored during analysis.

Standard compounds - discriminiation of standard samples and mixtures

Measurements of standard compounds were done to see if the FreshSense instrument could discriminate between the main classes of compounds (alcohols, sulfur compounds and amines) that form during spoilage of fish. In Table 2 is a list of the standard compounds that very studied.

Table 2. Standard compounds used to study the performance of an electronic nose.

Class of compounds	Compounds	Concentration in aqueous
Alcohols:	Methanol Ethanol, Propanol, Isopropanol, Butanol, 2-Butanol, Isobutanol, Pentanol, Isoamylalcohol	25-400 ppm
Esters	Ethyl acetate	50-200 ppm
Sulfur compounds	Dimethyldisulfide (DMDS), Dimethylsulfide (DMS):	5-25 ppm
Amines	Trimethylamine (TMA), Dimethylamine (DMA)	100-1000 ppm
Mixtures	DMDS/ Ethanol / TMA	5 ppm/20 ppm/200 ppm
	Ethanol/ Ethyl acetate	100 ppm /100 ppm

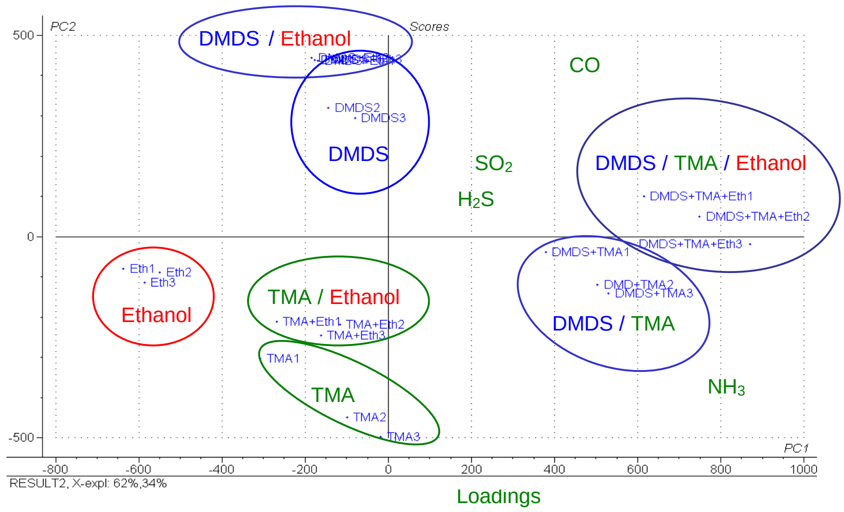


Figure 2. PCA analysis of FreshSense measurements of different concentrations of standard compounds and mixtures (ethanol, trimethylamine and dimethyldisulfide) (From the Masters Thesis of Aslaug Högnadóttir, 1999)

Figure 2 shows PCA analysis illustrating the ability of the FreshSense instrument to discriminate between various standard compounds and standard mixtures.
To successfully transfer the electronic nose from laboratory to industry, sampling techniques and calibration methods must be optimized. Moreover, it is very important to establish an easy to use calibration routine for the instrument.
There is a need for a rapid technique in the fish industry to evaluate the freshness of fish. Representatives from various parts of the fishery chain have expressed a need for a reliable, rapid technique. Different type of new instrumental techniques have shown promising results, however none of these have been successfully implemented in the industry. Sensory analysis is by far the most used technique in the industry and the challenge is to use electronic noses to replace the odour evaluation of the sensory analysis (9, 10).

iii) Preparation for Demonstration Consortium Meeting and other dissemination activities.

- Poster about the project was presented at an exhibition called "European Days 1998 in Iceland", sponsored by the The Icelandic Research Council, Nov. 13-15, 1998, Reykjavík, Iceland

IFL participated in the following events and disseminated results from the project:

- Electronic NOSE User Forum in Ispra Italy on June 17-18th, 1999, organised by the Network of Excellence on Artificial Olfactory Sensing
- Sensory Evaluation and Quality, Workshop VIII, Reykjavík, Iceland, September 9-11, 1999

At the workshop in Reykjavík, Iceland in September, the idea is to give electronic nose manufacturers an opportunity to display their instruments. This will be a good opportunity to demonstrate the Bloodhound instrument.

References

(1) Ólafsdóttir, G., and Fleurence, J. 1998. Evaluation of fish freshness using volatile compounds-Classification of volatile compounds in fish. *In* Methods to Determine the Freshness of Fish in Research and Industry, Proceedings of the Final meeting of the Concerted Action "Evaluation of Fish Freshness" AIR3 CT94 2283. Nantes Nov 12-14, 1997. International Institute of Refrigeration, 55-69 .

(2) Ólafsdóttir, G.. Application of gas sensors to monitor freshness of fish and fish products. In Proceedings from "Electronic Noses in The Food Industry" sponsored by SIK and MATFORSK , Stockholm, Sweden, 16. - 17. November, 1998.

(3) Ólafsdóttir, G., Högnadóttir,Á. and Martinsdóttir, E., 1998. Application of gas sensors to evaluate freshness and spoilage of various seafoods. *In* Methods to Determine the Freshness of Fish in Research and Industry, Proceedings of the Final meeting of the Concerted Action "Evaluation of Fish Freshness" AIR3 CT94 2283. Nantes Nov 12-14, 1997. International Institute of Refrigeration, 100-109.

(4) Ólafsdóttir, G., Martinsdóttir, E. and Jónsson, E. H., 1997. Rapid gas sensor measurements to predict the freshness of capelin (*mallotus villosus*). J.Agric. Food Chem. 45,7, 2654-2659.

(5) Ólafsdóttir, G.,Martinsdóttir, E. and Jónsson, E.H.. Gas sensor and GC measurements of volatile compounds in capelin (*Mallotus villosus*). In Seafood from Producer to Consumer, Integrated Approach to Quality. Eds. Luten, J. B., Börresen, T. and Oehlenschläger, J. Amsterdam, Elsevier (1997), 507-520.

(6) Ólafsson, R., Martinsdóttir, E. , Ólafsdóttir, G. , Sigfússon, Th.I. and Gardner, J.W. , 1992. Monitoring of fish freshness using tin oxide sensors. In "Sensors and Sensory Systems for an Electronic Nose", J.W. Gardner and P.N. Bartlett (Eds), Kluwer Academic Publ. 257-272.

(7) Jensen, B., Refsgaard, H.H.F., Ólafsdóttir, G. 1998. Headspace and extraction methods for analysis of volatile and semivolatile coumpounds in fish Chemical and sensory assessment of lipid-derived volatiles. *In* Methods to Determine the Freshness of Fish in Research and Industry, Proceedings of the Final meeting of the Concerted Action "Evaluation of Fish Freshness" AIR3 CT94 2283. Nantes Nov 12-14, 1997. International Institute of Refrigeration, 70-91.

(8) Högnadóttir, Á., Ólafsdóttir, G. and Martinsdóttir, E.. Optimization of sampling techniques and measurements for the electronic nose "FreshSense". 28th WEFTA meeting, October 4-7, 1998, Tromsö, Norway.

(9) Ólafsdóttir, G., Verrez-Bagnis, V., Luten, J.B., Dalgaard, P., Careche, M., Martinsdóttir, E., Heia, K., 1998. The need for methods to evaluate fish freshness. *In* Methods to Determine the Freshness of Fish in Research and Industry, Proceedings of the Final meeting of the Concerted Action "Evaluation of Fish Freshness" AIR3 CT94 2283. Nantes Nov 12-14, 1997. International Institute of Refrigeration 17-29.

(10) Ólafsdóttir, G., Martinsdóttir, E., Oehlenschläger, J., Dalgaard, P., Jensen, B., Undeland, I., Mackie, I. M., Henehan, G., Nielsen, J. and Nilsen H. 1997. Methods to evaluate fish freshness in research and industry. Trends Food Sci. Technol. August 1997, Vol. 8.

II. Progress report - 2nd year, 1999 - 2000

Application of Bloodhound Beta-Instruments (BH213) for Fish and Fish Products

1. Objectives

The main objective of this demonstration project is to manufacture a sensor array system for use in the food and drinks industry which overcomes the problems of water vapour interference, irreproducibility and lack of discrimination to volatile food components. In addition some progress towards tuned selectivity and relative quantitation will be addressed. The tasks in the project are diveded between technology developers and technology users, where IFL belongs to the latter group.

2. Actions in the project

Task 7 Demonstration.

The role of IFL in the project is to evaluate the use of the Bloodhound instrument for fish and fish products. This involves placement of beta-instruments at IFL and carrying out demonstration of instrumentation for fish (sub-task 7.1) and provide feedback on the effectiveness of the new instruments in 'real' applications. The data generated will be used to produce presentations ready for public dissemination through sub-task 7.2.

Sub-Task 7.1 **Internal Placements and Data Generation.**
Time Schedule: 21 months intermittent work, *start month 15 - end month 36*.

Sub-Task 7.2 **Dissemination Workshops.**

Estimated Time Schedule:	June/July 2000	Month 27
	November 2000	Month 32
	February/March 2001	Month 35

3. Planned Research Activities

Task 7.1 Internal Placements and Data Generation: The activities at IFL during the second period of the project have focused on testing the performance of two beta-prototypes of the Bloodhound instruments, one with polyconducting polymers and the other with DLC (discotic liquid crystal) sensors. Some initial testing has also been done with a new DLC based BH 213 unit delivered in December 1999.

4. Research activities during the second reporting period carried out by partner 4

4.1 Validation of the technology in terms of usefulness for fish applications

Sensory analysis is mainly used in the fish industry for fish freshness evaluation, but the need for instrumental methods for rapid detection of fish freshness has been expressed for years (Olafsdóttir *et al*., 1997a). A recent questionnaire on the need for methods to evaluate fish quality shows that the fish sector in Iceland agrees that rapid methods are needed to evaluate fish freshness in a rapid and objective way and similarly they strongly agree that a rapid instrument to determine the quality of fish is needed. (Tryggvadottir and Olafsdottir, 2000). These results are encouraging for further research and the development of new techniques to provide the industry with rapid instruments to detect fish freshness and quality. The questionnaire was conducted in 12 countries in Europe and was a collaboration of two current EU projects MUSTEC (Multisensor for Fish; CT98-4076) and FQLM (Fish Quality Labelling and Monitoring; CT98-4174).

The requirement of the industry is that techniques for quality and freshness evaluation should be rapid and non destructive and the instruments should be applicable on-line. Additionally the ultimate goal is to have handheld instruments that could be applicable for spot-checks. This is perhaps too ambitious and today the Bloodhound instrument, like many other electronic nose techniques, does not meet these requirements. The sampling is done in a closed sampling container and the instrument is essentially a laboratory instrument. For successful transfer of the technique from laboratory to industry, sampling techniques must be standardised and it is necessary to use closed containers and consistent temperature for reproducible sampling of volatile compounds in fish (Olafsdóttir, 1999). Therefore, the technique could only be implemented as an "at site" application rather than on-line technique for quality monitoring in the fish industry.

4.2 Experiments at IFL - The performance of two Bloodhound units (BH 213 and DLC) towards various fish products and characteristic standard compounds

The Bloodhound instruments were tested by performing series of experiments with standard compounds which are typically present during spoilage of fish i.e. trimethylamine, ethanol and other short chain alcohols. In addition fish products of different freshness and quality were measured.

4.2.1 Sampling

The dynamic sampling system of the Bloodhound instrument involves the use of glass vials (32 mL). The vials were cleaned with water and no soap was added because contamination of the sensors was noticed when soap was used. The cleaning of the

plastic tubing was troublesome and the smell of compounds like trimethylamine (TMA) was particularly evident.
When measuring salted fish fillets a closed plastic sampling bag was used with a special type of seal which can be used to insert the tubing for direct sampling into the Bloodhound instrument. Larger sample containers such as the plastic bags have some advantages because the sample preparation is minimal and whole pieces of fish can be measured directly. Some problems were encountered when using the plastic bags. The standardisation of the weight of the sample and the amount of air in packages is necessary to be able to quantify, but it is difficult to determine the total volume of air enclosed in the bag. Another disadvantage is that it is impossible to monitor the temperature of the sample. The measurements were done at room temperature and since the fish samples are most often stored at refrigeration temperatures, the higher room temperature influences the sample temperature rapidly, in particular if the sample is small. Temperature control of samples is necessary for reproducible measurements and meaningful quantification. The same temperature has to be used for measurements if the results are going to be compared. In our experiments the samples were allowed to reach room temperature in most cases before measurements started.

4.2.2 Measurements of water and standard compounds

Table 1. Measurements of series of standard compounds with Bloodhound instruments

Instrument	Standards (conc.)	Date
Bloodhound BH213	methanol 10^{-1} - 10^{-4}	19-07-99
	2-propanol 10^{-2} - 10^{-5}	02-08-99
	1-butanol 10^{-2} - 10^{-5}	28-07-99
	isoamylalcohol 10^{-1}- 10^{-5}	03-08-99
	TMA 10^{-1} - 10^{-5}	01-09-99
		17-09-99
		27-09-99
	ethanol 10^{-1} - 10^{-5}	28-09-99
Bloodhound DLC	ethanol 10^{-1} - 10^{-5}	24-08-99
	methanol 10^{-1} - 10^{-5}	24-08-99
	TMA 10^{-1} - 10^{-5}	01-09-99

Water analysis was done frequently during the period of testing. 25mL of distilled water were put in the sample and reference vials. The tubing flushing air is inserted into water so that air is purged through the water. Analytical grade standard compounds were obtained from Merck: trimethylamine 45%, methanol, propanol, butanol and isoamylacohol and ethanol 96% (vol/vol) from Lyfjaverslun Íslands hf. Table 1 lists the standard compounds measured and their concentrations. Samples were measured in triplicate.

4.2.3 Measurements of fish and fish products

Various quality of different fish products were measured such as salted fish, salmon fishmeal and haddock.

4.2.3.1 Measurements of salted fish and salmon

14g of salted fish mince and 22g of salmon mince (homogenised fillets) were put in the glass vials and compressed lightly to have approximately the same volume in the sampling vials each time. The temperature of the samples was 22-24°C during measurements and the reference sample was water using the same volume as the fish mince sample. The tubing was cut short and only purging the surface of the sample.

Plastic bags were used for sampling of whole fish fillets and approximately 950g of fish was weighted and put into the bags which were then sealed by using a heated string. The samples were allowed to equilibrate in the bags for half an hour before measurements started. The reference sample used was air (empty vial).

The salmon samples were judged putrid and fresh respectively by sensory classification and the TVN (total volatile nitrogen) content of the salted fish mince was measured.

Table 2. List of samples of salted fish and salmon measured with Bloodhound BH213 and DLC

Instrument	Sample #	Date	TVN mgN/100g
Bloodhound BH213 (polyconducting polymer sensors)	4353 salted fish mince	08-09-99	90
	4570 salted fish mince	08-09-99	20
	4663 salted fish mince	15-09-99	31,3
	4665 salted fish mince	15-09-99	34,2
	4569 salted fish mince	15-09-99	16
	4666 salted fish mince	16-09-99	35,4
	4353 salted fish fillet	16-09-99	90
	4666 salted fish fillet	16-09-99	35,4
	4363 2-5 putrid salmon	08-09-99	
	4360 2-2 fresh salmon	08-09-99	
Bloodhound DLC (discotic liquid crystal sensors)	4353 fish mince	15-09-99	90
	4570 fish mince	15-09-99	20

4.2.3.2 Measurements of fish meal

Plastic sampling containers (400mL) were modified by inserting the tubing in the lid and sampling was done directly from these. About 50 g of herring meal was weighted and the reference sample was water in the small glass vial.

Table 3. List of samples of herring meal measured with Bloodhound BH213 and DLC

Instrument	Sample #	Date
Bloodhound BH213	50g herring meal #1574	07-09-99
Bloodhound DLC	50g herring meal #1574	07-09-99

4.2.3.3 Measurements of haddock of different quality with Bloodhound BH213

A storage study of haddock was done at IFL. The fish was caught by long line and samples arrived at the laboratory one day later. The fish was gutted and iced in boxes and stored at 0-2°C for a period of 18 days. Fish was analysed on days 1, 4, 6, 8,11,13,15 and 18 during the period from September 26 until October 11. Approximately 20g of fish fillet was put into the glass vial and temperature of the sample was 20-22 °C during measurements. This study was a part of a larger study where various techniques were used to monitor the changes occurring during storage of fish in ice (Tryggvadottir and

Olafsdottir, 2000). One of the techniques used was an instrument with electrochemical gas sensors (FreshSense, Etherdata, Artorg 1, Saudarkrokur, Iceland) that was developed in Iceland and has been used in various research projects to monitor freshness and the onset of spoilage in fish and fish products (Olafsdóttir *et al*., 1997b,c, 1998).

4.3 Results and Discussion

The data was analysed using principal component analysis (PCA) using the software Unscrambler 6.1 (Camo A/S) and in most cases only the divergence was used. PCA is a good way to study the main trends in the data and to study the ability of the sensor array to discriminate between various standard compounds, different concentrations of the same compounds and fish products of different quality. In Appendix 1 is the raw data for all the measurements (divergence).

4.3.1 Measurements of standard compounds

Data from repeated measurements of water collected for one month with the Bloodhound BH213 unit is used to demonstrate the reproducibility of the measurements. Figure 1 shows the divergence of sensor #2 in the BH213 unit which was selected as a typical output from the sensor array. A decrease in response from the morning until the afternoon is observed on day 17.09.99. A series of TMA samples in different concentrations (10^{-05} - 10^{-01}) were measured on that day. It has been pointed out that amines may have poisoning effect on the sensors. This may in fact be a serious problem when measuring fish since TMA (trimethylamine) is typically formed in high concentrations during storage of fish. Poisoning of many of the sensors was observed, a few sensors(# 2,3,4) showed decreased response while other sensors showed a dramatic increase in response to distilled water (sensors 1,6,11,12 showed 1000 times increase in response). The poisoning effect was consistent for several days (i.e. 15 days for the sensor #12). These measurements show that poisoning of sensors caused by TMA is a serious problem.

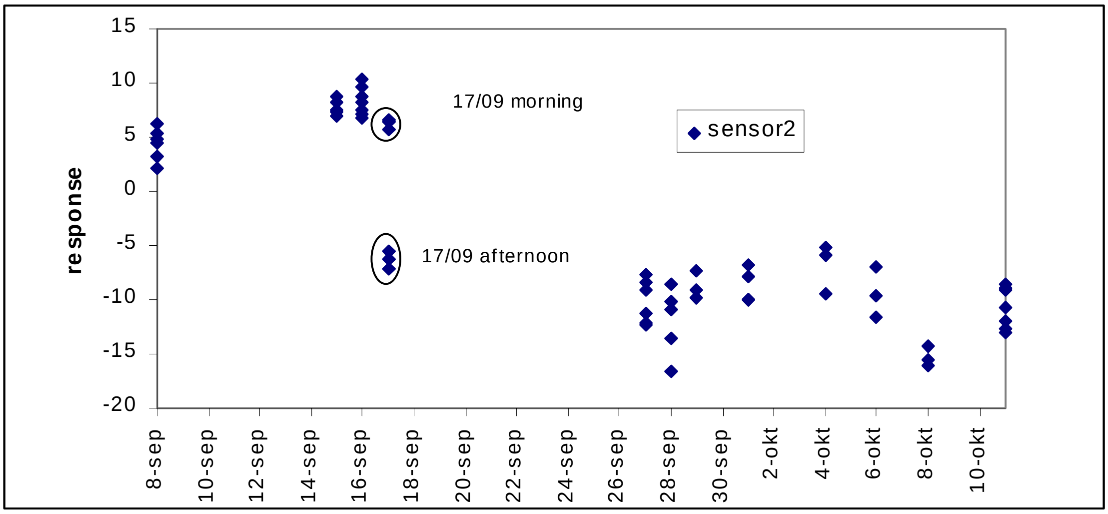


Figure 1. Divergence of sensor No. 2 in Bloodhound BH213 when measuring water samples during one month

Decreased stability in the measurements with Bloodhound BH213 was also observed over time. In the beginning it was possible to fix a 10% accepted range but over time this has changed to 30% between measurements to make the analysis finish in a reasonable time.

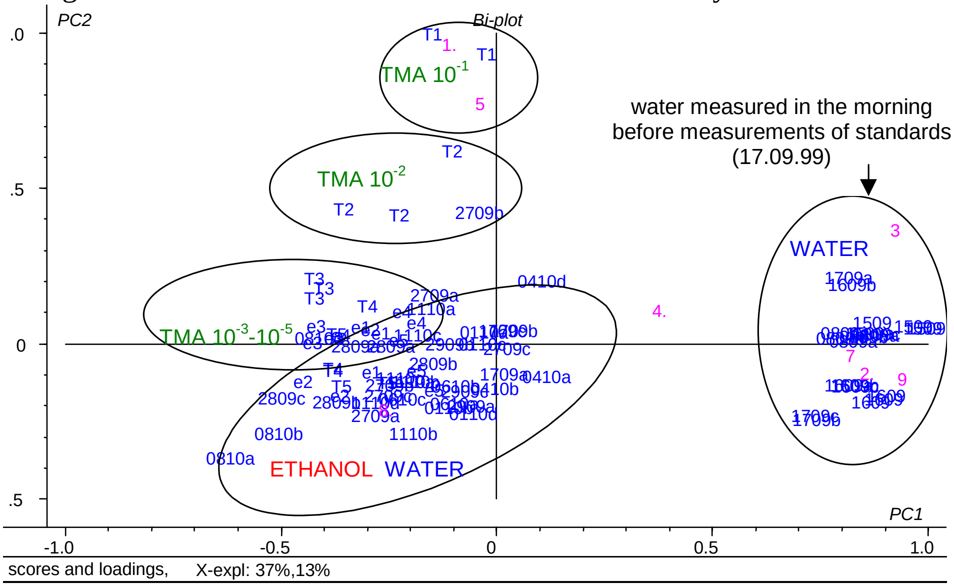


Figure 2. PCA analysis of Bloodhound BH213 data (divergence) of water measurements performed during the period from August – October ´99. TMA was measured on the 27.09.99 and ethanol measured the 28.09.99. Water measurements are identified by the date, TMA and ethanol by a "T" and a "e" respectively, followed by the concentration ($1=10^{-01}$). Loadings of nine sensors are shown as numbers.

To study further the reproducibility of the measurements, data from measurements of water and standard compounds (TMA and ethanol) are compared using PCA analysis.

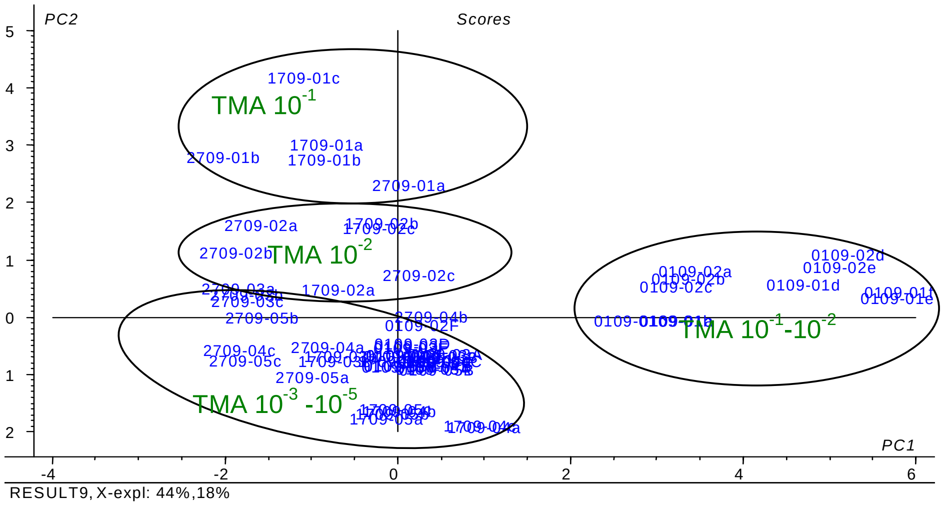


Figure 3. PCA analysis of the data (divergence) from a series of measurements of different concentrations of TMA (trimethylamine) measured in September (TMA 10^{-1} - 10^{-5}, 01-09-99;17-09-99; 27-09-99) with the Bloodhound BH213 unit.

Figure 2 shows a PCA scores plot of repeated measurements of water, TMA and ethanol with Bloodhound BH213. The pollutioning of the sensors during the analysis of TMA is perhaps influencing the poor discrimination of ethanol and water measured the next day. High concentration of TMA (10^{-01} - 10^{-02}) are discriminated on the PCA plot.

Figure 4 shows a PCA plot of repeated measurements of water, TMA and ethanol with the DLC unit. This unit appears to be able to discriminate between varying concentrations of TMA samples (10^{-01} - 10^{-05}) and also to discriminate between each standard and water. However for ethanol no trend is observed, although the distinction between water and ethanol sample is clear. Water samples are mostly grouped together in this model however when compared to salted fish the grouping of the same water samples is not as clear (see later). During these measurements it was necessary to set an acceptable range of 30% between measurements to make the analysis finish in a reasonable time.

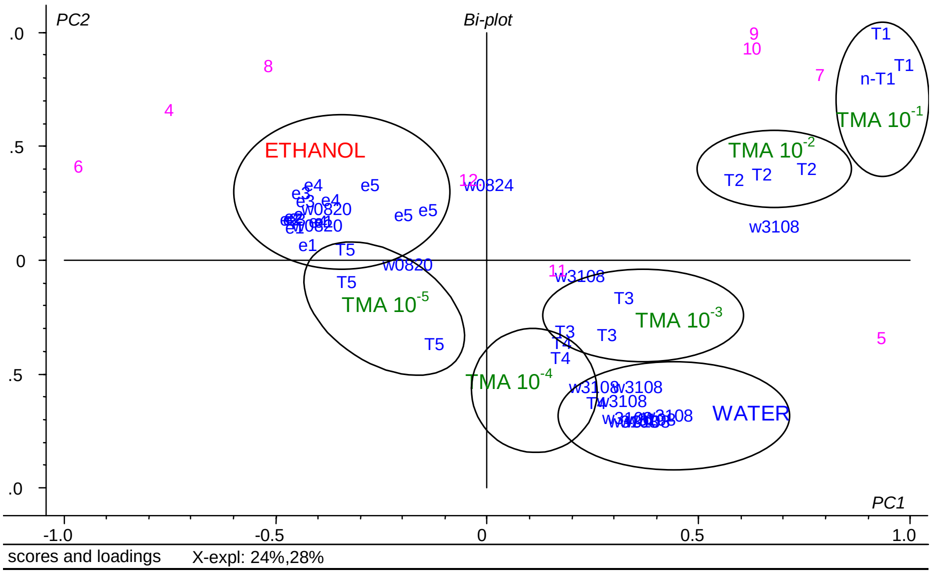


Figure 4. PCA analysis of data (divergence) of water measurements from 20.08.99 to 31.08.99 during different days using the DLC unit. TMA was measured the 27.09.99 and ethanol was measured on the 24.08.99. Water measurements are identified by the date, TMA and ethanol by a "T" and "e" followed by the concentration ($1=10^{-1}$). Loadings of the sensors are shown as numbers.

Figure 5 shows a PCA plot of the results from measurements of alcohols of different chain length using the Bloodhound BH213. A clear grouping of the compounds analysed is not obvious and only in some cases a trend in the data is observed based on the concentration of compounds.

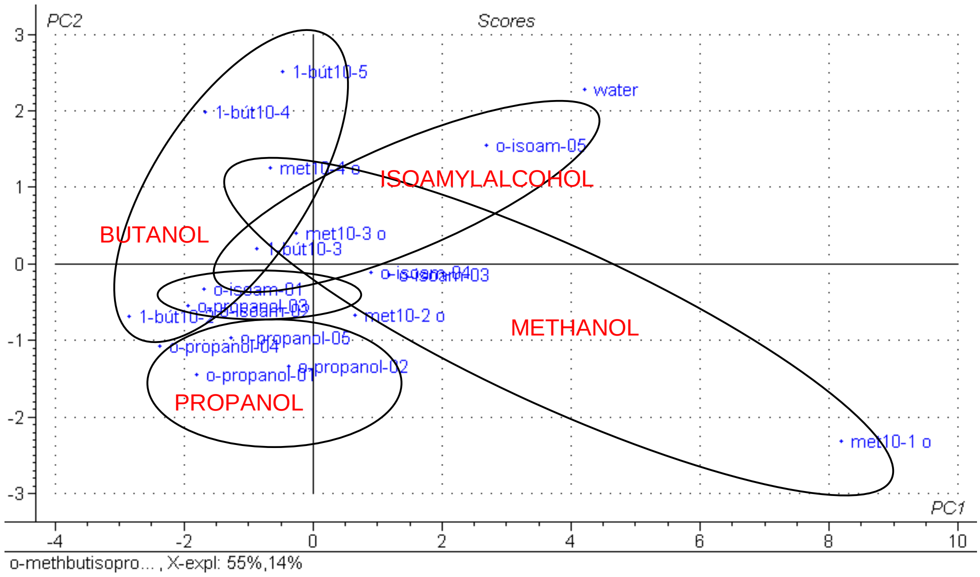


Figure 5. PCA analysis of the Bloodhound BH213 data (divergence) from a series of measurements of different concentrations of standard compounds performed in July and August (methanol 10^{-1}-10^{-4}, 19-07-99; 2-propanol 10^{-2}-10^{-5} , 02-08-99; 1-butanol 10^{-2} - 10^{-5}, 28-07-99; isoamylalcohol 10^{-1}-10^{-5}, 03-08-99)

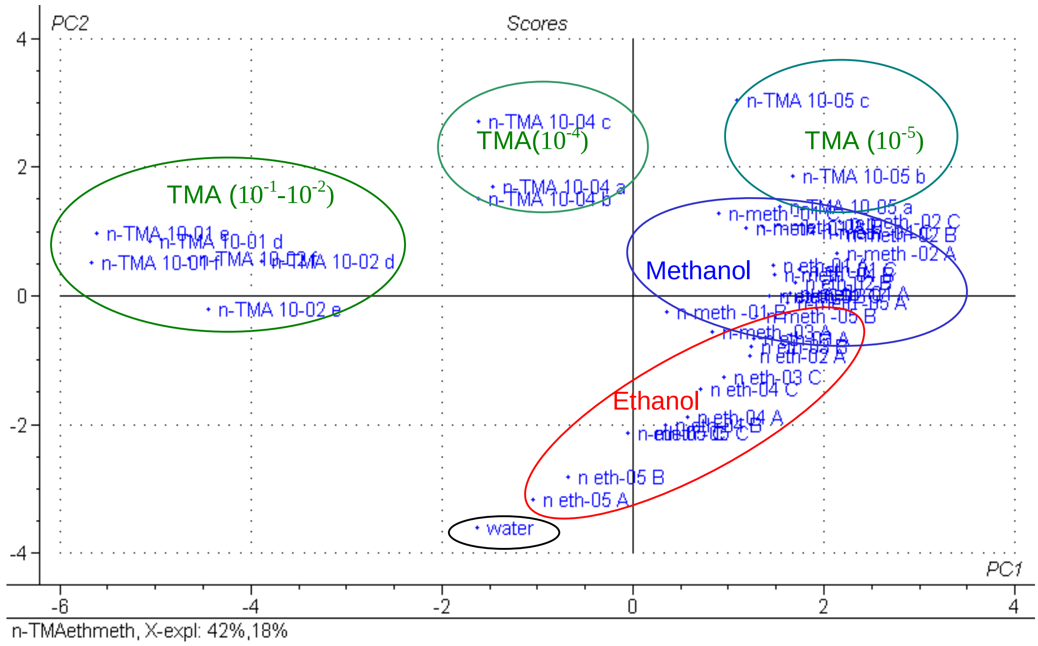


Figure 6. PCA analysis of the Bloodhound DLC data (divergence) from a series of measurements of different concentrations of standard compounds performed in August and September (ethanol 10^{-1} - 10^{-5}, 28.09.99; methanol 10^{-1} - 10^{-5}, 24.08.99; TMA 10^{-1} - 10^{-5}, 01.09.99)

Figure 6 shows a PCA plot of TMA, ethanol and methanol. TMA is well discriminated from the other compounds and water and the different concentrations of TMA can be discriminated on the PCA plot. This trend is also observed for ethanol even if the distinction between the concentrations is less evident and low concentrations overlap with data from methanol.

4.3.2. Measurements of fish and fish products

Various quality of different fish products were measured such as fishmeal, salted fish salmon and haddock

4.3.2.1 Measurements of salted fish (fish mince) with Bloodhound BH213

Figure 7 shows a PCA plot with data from measurements of two salted fish samples with different TVN (total volatile nitrogen) value. TVN is traditionally used in the fish industry as a quality index to evaluate the spoilage of fish. The samples were analysed with the BH213 instrument and the result show that samples of different spoilage level are separated on the PCA plot. However, additional measurements of samples of different quality analysed later on did not confirm these results. Figure 8 is a PCA plot of combined data of salted fish samples of different quality measured during several days. It is possible to see that the two samples analysed the first day (TVN=20 and 90 mg N/100g) do not follow the same trend based on increasing TVN values as the other samples (TVN=16, 31.3, 34.2, 35.1). It appears that samples are grouped together based on days of analysis rather than spoilage level of samples. However, a logical trend in the data based on TVN values within each day can be observed.

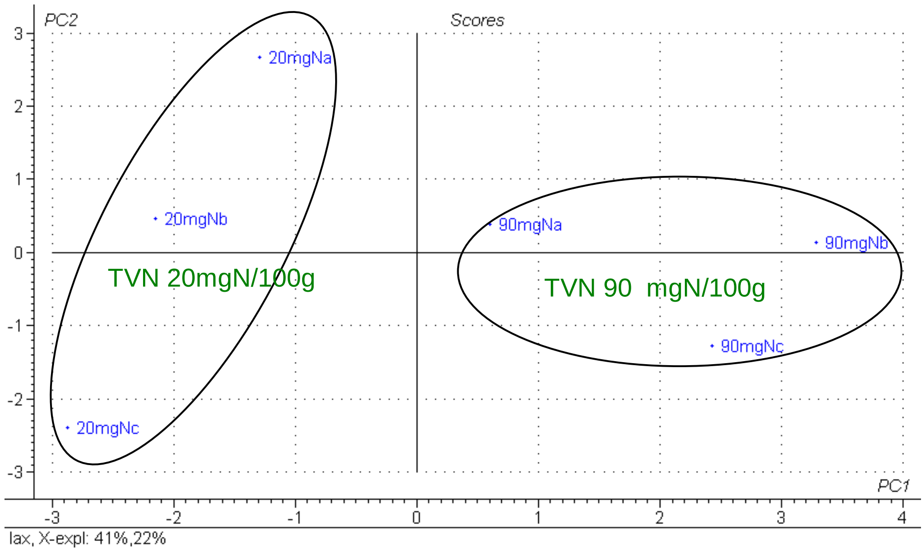


Figure 7. PCA analysis of the Bloodhound BH213 data (divergence) from measurements of salted fish of different quality (TVN= total volatile nitrogen) measured on September 8.

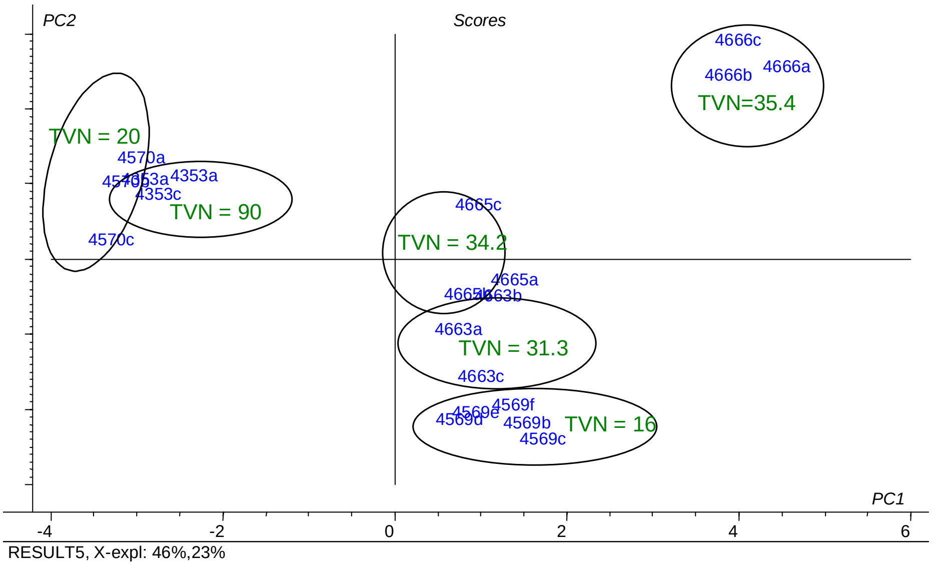


Figure 8. PCA analysis of the Bloodhound BH213 data (divergence) from measurements of salted fish of different quality (TVN= total volatile nitrogen mg N/100g) Measured on Sept 8, 15 and 16.

4.3.2.2 Measurements of salted fish (fish mince) with Bloodhound DLC

Two samples of different quality of salted fish (20mg N/100g and 90mg N/100g) were analysed during the same day with DLC instrument and the result were compared with water measurements before, between and after analysis of fish samples and also with water measured some days before. Water measurements are not consistent and appear to drift considerably during the same day and measurements done on different days do not agree (Figure 9).

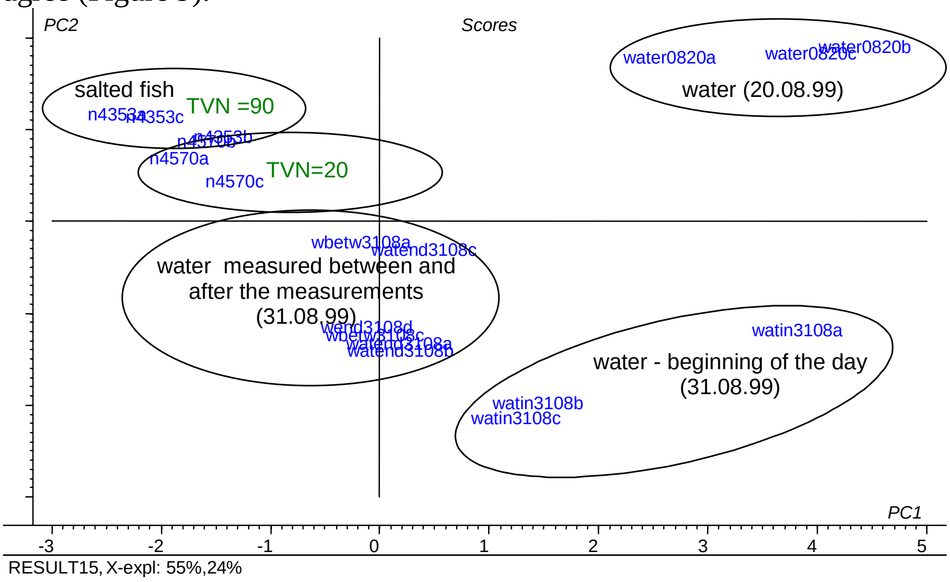


Figure 9. PCA analysis of the Bloodhound DLC data (divergence) from measurements of salted fish of different quality, samples 4353 (TVN=90) and 4570 (TVN=20) and measurements of water (Aug 31) done before, in between and after measurements of fish samples and one week earlier (Aug 20).

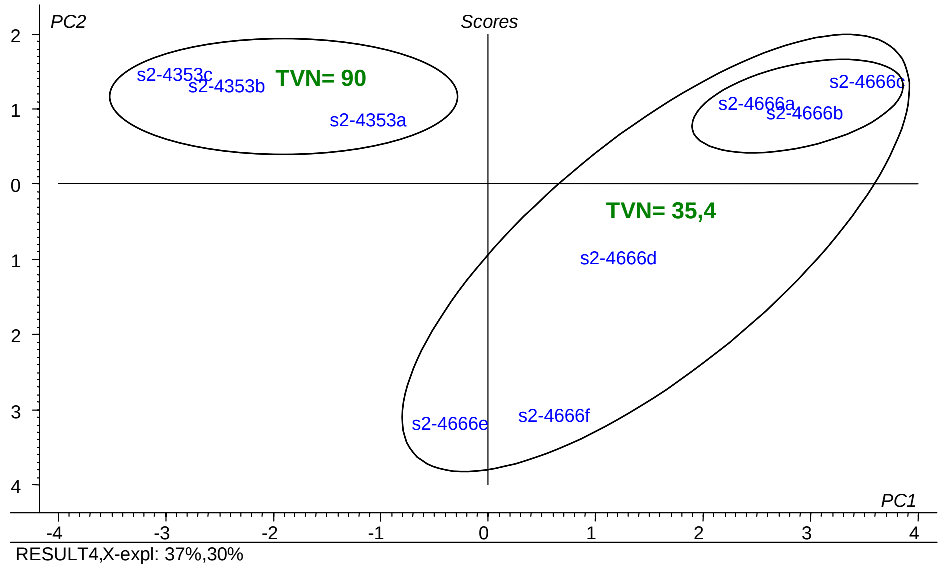


Figure 10. PCA analysis of the Bloodhound BH213 data (divergence) from measurements of salted fish fillets of different quality samples 4353 (TVN=90) and 4566 (TVN=35,4) measured on Sept 16.

4.3.2.3. Measurements of salted fish whole fillets with Bloodhound BH213

Plastic bags were used for sampling of 950g piece of fillet in each case and measurements were repeated. Figure 10 shows the corresponding PCA plot and the grouping of samples based on TVN values is observed, however there is a large drift in the data of repeated measurements of the same sample. This may be because the sample is changing with time rather than drifting of the sensors, since the same sample was used for repeated measurements.

4.3.2.4. Measurements of salmon of different quality with Bloodhound BH213

Figure 11 shows a PCA plot of three measurements of two salmon samples, one judged putrid and one fresh by sensory evaluation. Here a clear separation of the two samples is observed, but additional measurements of salmon of different quality are needed to verify these results.

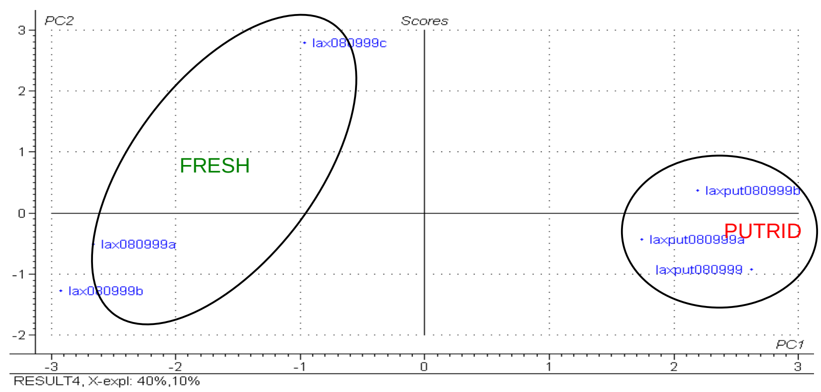


Figure 11. PCA analysis of the Bloodhound BH213 data (divergence) from measurements of salmon mince of different freshness

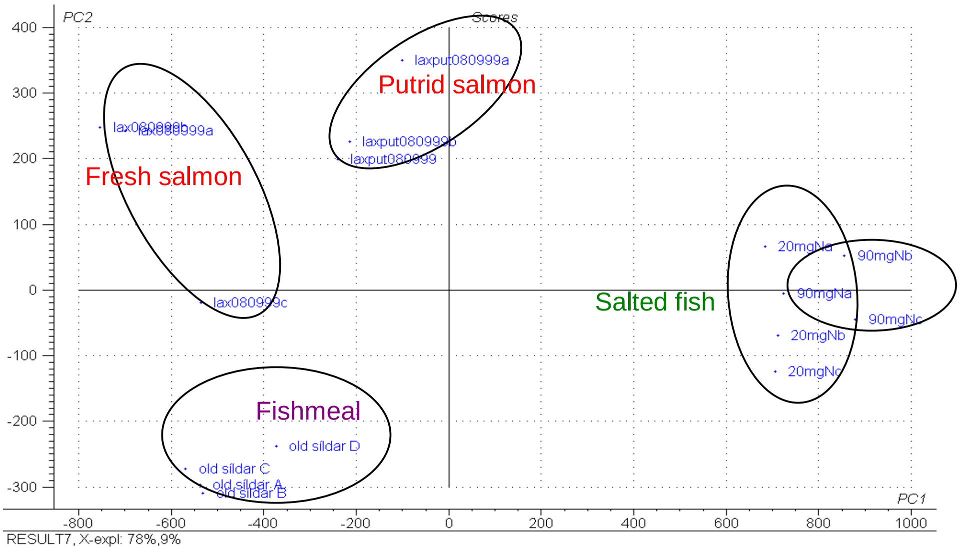


Figure 12. PCA analysis of Bloodhound BH213 measurements of salmon, fishmeal, salted fish (all variables – divergence)

4.3.2.5 Measurements of fish meal compared with measurement of different fish products with Bloodhound BH213

Figure 12 shows a PCA plot of all data from different fish products measured with the BH 213 unit. The different samples are well separated, but no discrimination between fish meal samples of different quality is observed.

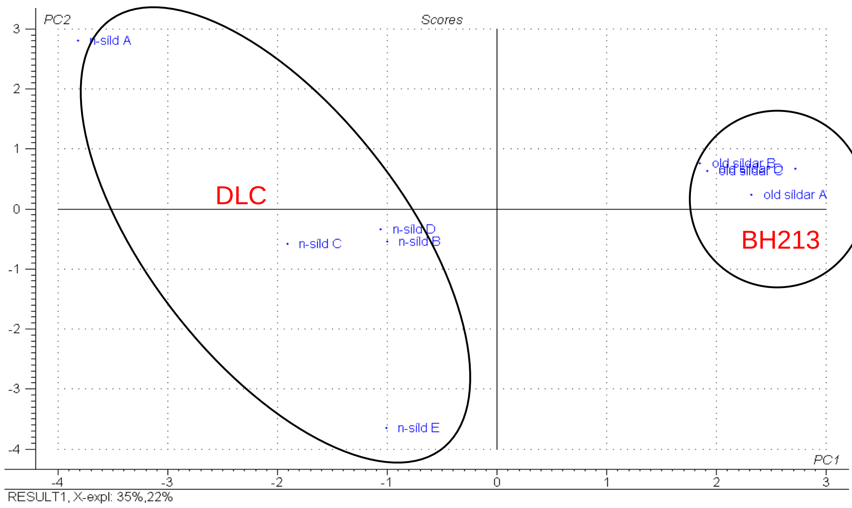


Figure 13. PCA scores plot of repeated measurements of fish meal using the Bloodhound BH213 and the DLC units.

4.3.2.6 Comparison of measurements of fish meal with Bloodhound DLC and the BH213

The PCA analysis of data from the same sample with the two instruments was done to demonstrate the repeatability of the different instruments (Figure 13). The repeatability of the measurements appear to be better when using the BH213 unit, since the data forms a more dense cluster. During the analysis of these samples it was possible to fix an acceptable difference between repetitions at 10% with BH213 and 30% with DLC which shows the different stability of the two instruments.

4.3.2.7. Measurements of haddock of different quality with Bloodhound BH213

Figure 14 shows a PCA plot with data from the storage study of haddock. The results do not show any clear discrimination between days and the overall trend is chaotic. The level of volatile compounds present in fish fillets is very low and apparently the sensitivity of the sensors is too low to detect the changes occuring in the fillets.

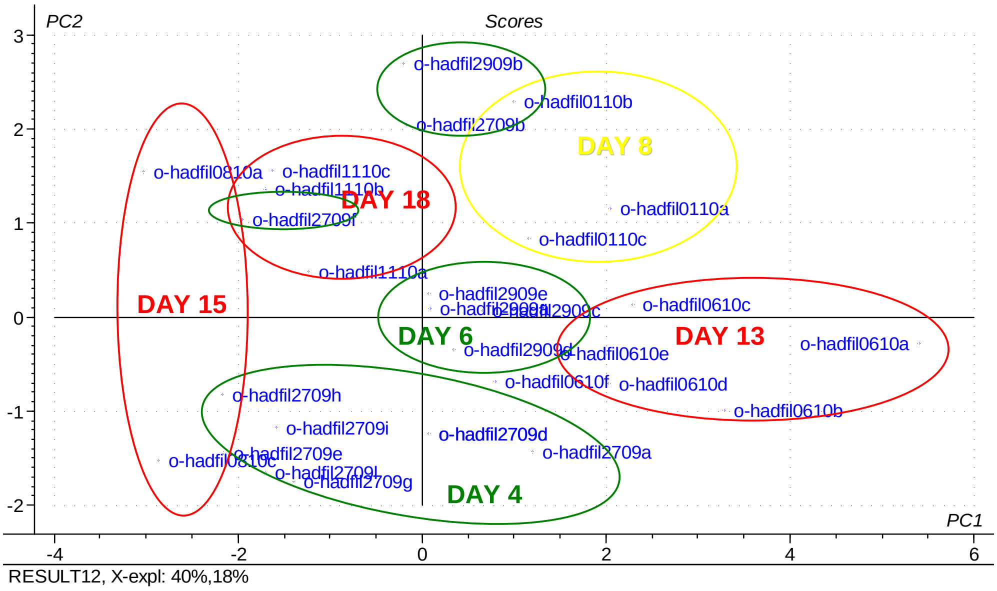


Figure 14. PCA analysis of data from haddock experiment performed in September with the BH213 instrument

For comparison a PCA biplot of data from the electronic nose FreshSense for haddock fillets are shown in Figure 15. Samples are grouped together according to days of storage. The first two PCs describe 78% and 14% respectively, of the variation of the samples. The samples from days 1, 4 and 6 are grouped together on the left side of the plot and the spoilage level or days of storage increases from left to right. The CO sensor is mainly influencing the first PC and the grouping of samples according to storage time is evident. The samples from day 11 had the highest response for the CO sensor and are therefore located furthest to the right on the plot. The samples from day 13 and 15 had lower CO responses, but slight increase in responses for the other sensors and are therefore grouped together. Figure 15 shows that the FreshSense instrument can discriminate between days when spoilage signs are present but discrimination between the first six days is not possible. The discrimination of the samples according to days is not always clear and samples from different days are close to each other on the plot. Temperature of samples was allowed to increase between repeated meaurements to study the effect of sample temperature on the response of the sensors. The effect of temperature is considerable and better discrimination between days would be achieved if the same temperature was always used during measurements. These results are also of importance when measuring with the Bloodhound instruments and the increasing temperature is most likely also affecting the response of the sensors in a similar way.

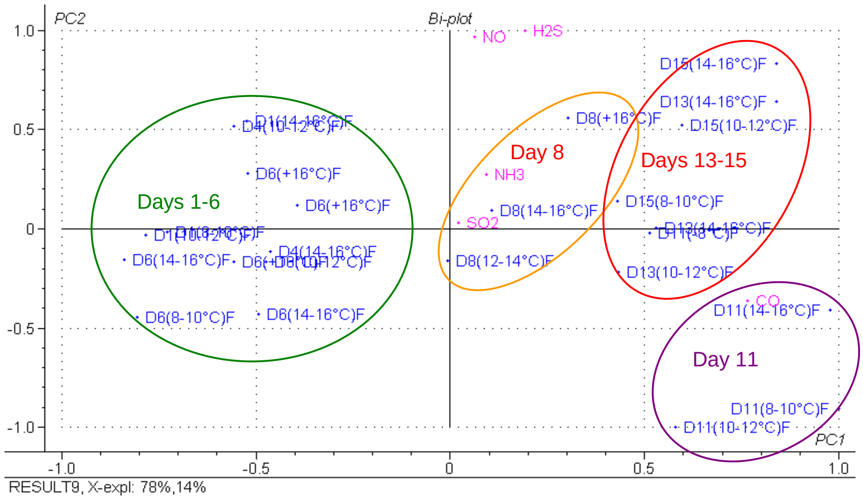


Figure 15. PCA biplot of FreshSense measurements of haddock fillets after storage in ice. Sample scores are shown in blue and labeled with storage day and temperature range during measurement. The variable loadings are shown in pink (CO, H_2S, NO, SO_2 and NH_3 sensors).

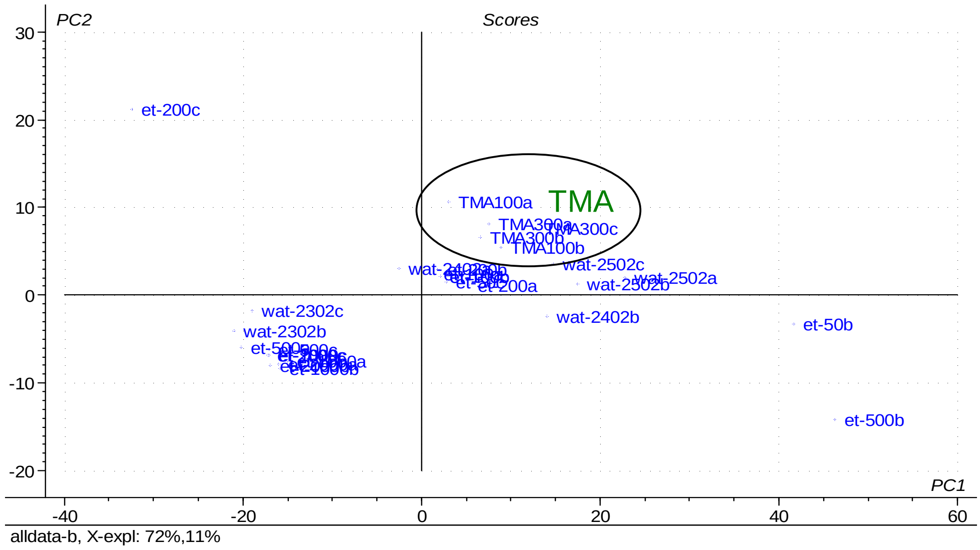


Figure 16 PCA plot of TMA, ethanol and water measurements with the new BH213-DLC unit

Figure 16 shows the results from repeated measurements of TMA, ethanol and water with the new BH213-DLC unit. TMA data (100 and 300 ppm) appears to cluster together, but the instrument was not able to measure high concentration of TMA (500 ppm). The water and ethanol data is overlapping and no discrimination is observed. Water measurements are not consistent and these initial measurements show that the performance of the new unit is not better than the old instruments. The use of NaBr solution to control the humidity did not improve the performance of the instrument.

4.3.3. Conclusions

Measurements of standard compounds show that both the BH213 instrument with polyconducting polymer sensors and the DLC based instruments are able to discriminate between ethanol and TMA. Some trend based on increasing concentrations of the standards is observed. Poisoning of the sensors is observed after measuring amines and a long recovery time of the sensors was noticed. This may be a serious problem if the instrument is going to be used to detect spoilage of fish because fish typically has high levels of amines during spoilage. Measurements of water are not consistent and the inconsistency is mostly related to the poisoning of the sensors when analysing high concentrations of standard compounds or samples with high levels of i.e. amines like the salted fish. It also appears that measurements done within short time are more similar than measurements performed within longer time frame, indicating drifting of sensors.
Measurements of salted fish samples with the BH213 unit appeared to give promising results initially, since the samples were separated based on the TVN value. However, when measuring additional samples of salted fish and combining data from numerous days, the grouping of samples was mainly based on different days of analysis rather that TVN content of the samples. However, logical trend in the positioning of the data on the PCA plot was observed within each day of analysis.
The overall performance of the instruments is very much dependent on what kind of samples have been analysed prior to each measurement. The slow recovery of sensors after having been exposed to high concentration of standard compounds or samples with high levels of volatiles is troublesome and limits the use of the instruments.
Initial testing of the new BH213 unit shows that the sensitivity and discrimination power of the instrument appears to be inferior to the old instruments and therefore further development of the sensors is needed.

References

G. Ólafsdóttir, E. Martinsdóttir, J.Oehlenschläger, P. Dalgaard, B. Jensen, I. Undeland, I. M. Mackie, G. Henehan , J.Nielsen and H. Nilsen. 1997a. Methods to evaluate fish freshness in research and industry. Trends Food Sci. Technol. August 1997, Vol. 8. 258- 265.

G. Ólafsdóttir, E. Martinsdóttir and E. H. Jónsson, 1997b. Rapid gas sensor measurements to predict the freshness of capelin (*mallotus villosus*). J.Agric. Food Chem. 45,7, 2654-2659.

G.Ólafsdóttir, E. Martinsdóttir and E.H. Jónsson, 1997c. Gas sensor and GC measurements of volatile compounds in capelin (*Mallotus villosus*). In Seafood from Producer to Consumer, Integrated Approach to Quality. Eds. Luten, J. B., Börresen, T. and Oehlenschläger, J. Amsterdam, Elsevier, 507-520.

G. Ólafsdóttir, Á. Högnadóttir and E. Martinsdóttir, 1998. Application of gas sensors to evaluate freshness and spoilage of various seafoods. *In* Methods to Determine the Freshness of Fish in Research and Industry, Proceedings of the Final meeting of the Concerted Action "Evaluation of Fish Freshness" AIR3 CT94 2283. Nantes Nov 12-14, 1997. International Institute of Refrigeration, 100-109.

G. Ólafsdóttir, 1999. Initial performance report - March 1999 - Partner 4 Icelandic Fisheries Laboratories. Electronic Profiling of Food and Beverage Odour for Quality Determination, PROFILE- QD PL97-3436.

S. V. Tryggvadóttir and G. Olafsdóttir, 2000. Multisensor for fish: Questionnaire on quality attributes and control methods -Texture and electronic nose to evaluate fish freshness. Project report for the European Commission (Devolopment of multi- sensor techniques for monitoring the quality of fish, CT-98-4076). RF report 04-00.

5. Significant difficulties or delays experienced during the reporting period

Delay in the delivery and poor performance of the DLC beta-instrument has been of major concern resulting in limiteded time to test the instrument and produce reliable results to present at the first workshop. Problems encountered when initialising the new unit i.e. software failure and bad connections has caused further delays. Moreover the initial measurements with the new unit are not promising and problems related to stability of measurements including poisoning of the sensors and poor reproducibility of measurements are still of concern. Therefore, further development of the DLC sensors is needed before this technique can be applied successfully in an electronic nose.

6. Dissemination of results

IFL participated in the following events and disseminated partial results from the project:

- Electronic NOSE User Forum in Ispra, Italy on June 17-18th, 1999, organised by the Network of Excellence on Artificial Olfactory Sensing
- Sensory Evaluation and Quality, Workshop VIII, Reykjavík, Iceland, September 9-11, 1999 (see copy of overheads in Appendix 2)

Acknowledgements

Thanks to my colleagues Luca Laghi and Sigrún Jónsdóttir who have done the measurements and the PCA data analysis.

Appendix 1

Raw data from measurements

1) Divergence data for measurements of water with BH 213 unit
2) Divergence data for measurements of standards with BH 213 unit
3) Divergence data for measurements of salted fish samples with BH 213 unit
4) Divergence data for measurements of salmon, fishmeal and salted fish samples with BH 213 unit
5) Divergence data for measurements of water with DLC unit
6) Divergence data for measurements of standards with DLC unit
7) Divergence data for measurements of salted fish with DLC unit
8) Divergence data for measurements of haddock samples with BH 213 unit
9) Divergence data for measurements of water and standards with BH213 new DLC unit.

Divergence data for measurements of water with BH 213 unit

	1/Div.	2/Div.	3/Div.	4/Div.	5/Div.	6/Div.	7/Div.	8/Div.	9/Div.	10/Div.	11/Div.	12/Div.
o-watbetw0809a	4,045	4,396	4,267	3,17	6,585	7,087	6,261	-2,571	22,787	5,001	8,591	3,423
owatbetw0809b	2,927	4,8	4,936	-5,143	6,58	6,502	5,944	5,689	18,552	4,31	-6,647	3,158
o-watbetw0809c	3,752	6,251	4,34	4,727	7,303	6,979	7,531	3,384	16,622	5,293	7,963	2,994
o-watend0809a	2,163	5,43	3,413	5,913	6,041	6,035	4,833	4,226	13,507	2,087	-8,156	-1,868
o-watin0809a	4,136	3,286	3,799	1,689	5,333	18,518	6,82	-5,671	-19,55	2,889	-9,654	-2,173
o-watin0809b	4,535	2,119	3,24	1,602	8,37	11,373	4,88	-4,66	-14,56	-4,313	-81,89	-7,572
o-waft4663-1509a	6,886	8,21	6,126	10,085	8,687	10,093	32,973	-13,64	-28,14	2,71	-76,66	-4,158
o-waft4663-1509b	8,449	7,54	4,931	12,187	10,306	227,63	31,581	-15,22	-29,09	-2,895	-83,9	-4,732
o-waft4663-1509c	10,767	7,297	4,655	12,462	10,162	230,91	31,677	-16,29	-29,36	-3,153	-85,13	-5,018
o-waft4663-1509d	10,112	7,045	5,611	10,827	10,27	246,24	28,737	-17,11	-32,02	-3,313	-89,01	-5,226
o-wbetw1509a	7,001	8,793	5,397	10,243	8,881	9,153	35,093	-13,31	-29,18	-4,077	-74,36	-5,41
o-waft4666-160999a	9,576	10,324	5,536	21,973	-25,3	-47	28,674	-28,76	-32,62	-5,299	-77,41	-76,83
o-waft4666-160999b	8,614	8,799	5,374	21,722	-26,47	117,53	28,923	-22,27	-32,96	-4,821	-77,42	-79,9
o-waft4666-160999c	7,497	9,713	5,911	22,793	-24,09	68,206	30,345	-17,79	-32,17	-4,631	-77,38	-81,14
o-wend1609a	28,202	7,116	5,794	26,113	-21,66	1319	29,984	-11,44	-36,74	-2,164	-84,12	-89,43
o-wend1609b	28,818	6,806	5,637	25,779	-21,28	2482,1	32,823	-9,418	-35,63	-1,956	-85,1	-89,83
o-wend1609c	39,082	7,571	5,669	25,874	-21,51	1579,3	30,67	-10,77	-35,53	-2,287	-84,33	-90,82
o-watin160999b	8,239	8,291	5,437	21,831	32,359	63,206	27,405	-30,55	-29,38	-5,919	-72,26	-65,58
o-watin1709a	105,25	6,581	10,08	18,991	34,974	139,29	21,386	-7,857	-31,74	-11,99	-80,28	-72,63
o-watin1709b	120,51	5,797	8,123	18,732	-38,15	173,03	-23,06	-13,4	-33,83	-8,121	-83,47	-75,62
o-watin1709c	121,44	6,378	8,068	18,257	-35,69	763,4	-23,87	-13,63	-34,65	-8,682	-84,36	-76,87
o-wend1709a	-95,2	-7,179	-8,233	-18,46	-9,885	455,4	-35,7	-32,46	-47,06	5,002	565,87	-94,13
o-wend1709b	603,62	-5,451	-8,465	-16,25	12,327	563,02	-34,84	-27,96	-46,93	5,219	928,57	-93,25
o-wend1709c	559,33	-6,305	-8,428	-17,14	12,77	617,49	-36,67	-32,39	-46,96	4,109	342,18	-93,34
o-watend2709a	1245,1	-11,25	-10,35	-31,59	-17,01	720,67	-34,81	227,4	-70,46	-5,576	259,27	-99,99
o-watend2709b	-99,46	-12,08	-11,28	-31,79	-8,963	3657	-34,97	-50,72	-68,82	-3,788	412,83	-99,99
o-watend2709c	-99,44	-12,31	-11,4	-30,11	-14,7	900,22	-35,21	-48,81	-69,06	-3,551	916,11	-99,99
o-watin2709a	412,84	-8,453	-8,262	-27,97	-12,9	2122,7	-25,05	-78,54	-75,13	64,503	499,77	-85,35
o-watin2709b	2100,5	-7,704	-8,3	35,47	26,34	933,08	-24,97	-69,24	-74,2	60,131	1879,5	-86,42
o-watin2709c	816,4	-9,139	-8,547	51,104	21,965	2216,5	-24,86	-66,05	-74,18	-37,83	730,02	-87,76
o-watend2809a	498,3	-13,55	-13,38	-22,85	10,013	382,28	-34,64	86,461	-66,68	3,729	807,36	-99,97
o-watend2809b	-95,95	-16,66	-13,27	-26,21	-15,19	221,56	-36,17	48,744	-67,57	-2,224	-99,09	381,66
o-watin2809a	-99,06	-10,95	-10,16	-26,87	15,859	636,09	-32,68	153,63	-68,36	-6,51	478,73	-99,18
o-watin2809b	Inf	-8,603	-9,15	44,621	13,028	1725	-31,29	598,05	-66,87	-8,082	2136,9	-99,18

o-watin2809c	-98,3	-10,09	-9,966	-24,08	12,924	175,67	-32,93	1391,9	-66,61	5,318	966	1496,6
o-watin2909a	-91,25	-7,357	-8,229	-24,78	-14,13	332,91	-29,73	39,868	-64,25	-11,82	258	-94,96
o-watin2909b	-94,41	-9,061	-8,294	-28,27	16,249	407,95	-29,07	69,523	-62,38	-9,357	124,99	-96,8
o-watin2909c	-96,42	-9,826	-8,177	-24,45	-11,69	1364,4	-30,27	-60,59	-61,98	-8,285	442,13	-97,35
o-watin0110a	442,59	-6,837	-6,978	20,238	14,088	-70,98	-27,62	382,82	-60,91	7,559	493,19	-98,77
o-watin0110b	-94,77	-10,06	-8,392	-21,57	-14,3	627,77	-28,81	185,62	-59,57	-6,616	315,71	-99,55
o-watin0110c	298,08	-10,07	-9,069	33,14	12,922	361,6	-29,24	143,43	-58,96	-7,799	372,72	831,19
o-watin0110d	465,58	-7,915	-8,981	27,269	-15,56	273,7	-30,11	364,46	-61,04	-7,562	760,26	760,26
o-watin0410a	473,62	-5,12	-6,975	34,108	-16,93	206,88	-26,38	134,51	-58,67	11,08	277,04	-96,93
watin0410b	298,19	-9,483	-7,631	-19,39	-10,11	490,26	-28,44	-49,4	-54,97	-8,835	261,36	-99,04
o-watin0410d	558,1	-5,819	-6,177	24,815	32,476	629,9	-26,15	90,429	-55,04	6,91	290,15	-98,77
o-watin0610a	413,07	-9,681	-8,371	-23,28	-12,35	169,73	-28,03	70,773	-63,9	-12,12	284,56	-98,45
o-watin0610b	1284,8	-6,98	-7,984	-24,61	-13,64	243,75	-28,46	207,55	-64,39	9,224	364,26	-98,92
o-watend0610c	-91,66	-11,54	-10,67	-25,18	-12,49	1858,9	-37,94	60,874	-62,21	-5,438	-94,68	102,1
o-watin0810a	390,57	-16,05	-13,93	-29,42	-21,29	441,53	-47,65	552,4	-81,91	-18,17	-98,33	133,71
o-watin0810b	489,28	-15,48	-14,27	-31,1	-20,99	1044,2	-47,55	67,372	-81,47	-16,69	-98,39	656,14
o-watin0810c	-92,36	-14,27	-14,07	34,003	21,418	303,97	-47,23	141,89	-81,5	-14,62	327,61	-99,97
o-watin1110a	-87,49	-8,961	-9,406	27,143	31,601	422,99	-35,17	123,24	-74,36	-10,88	629,84	140,62
o-watin1110b	-90,4	-8,519	-9,678	-26,74	-18,64	896,15	-35,4	77,896	-74,7	-23,26	-96,6	539,75
o-watin1110c	863,95	-9,085	-9,853	-19,11	-12,01	205,08	-38,26	79,985	-72,49	7,195	598,92	-99,95
o-watin1110d	603,66	-11,96	-10,51	-24,87	-14,32	310,65	-36,41	70,416	-74,47	-7,324	-96,54	564,42
o-watend1110a	92,374	-13,02	-9,767	30,903	-16,05	299,53	-34,98	120,94	-73,55	4,19	-97,6	122,64
o-watend1110b	846,65	-12,76	-10,54	22,256	-12,72	697,11	-36,34	-49,23	-74,13	-4,923	-97,29	115,2
o-watend1110c	206,2	-10,78	-10,31	40,696	13,948	179,08	-36,2	175,96	-73,53	-3,686	218,27	-99,92

Divergence data for measurements of standards with BH 213 unit

	1/Div.	2/Div.	3/Div.	4/Div.	5/Div.	6/Div.	7/Div.	8/Div.	9/Div.	10/Div.	11/Div.	12/Div.
TMA0109-01a	2,957	145,31	41,321	7,043	4,944	5,658	14,394	26,409	31,929	4,454	-1,401	-3,214
TMA0109-01b	-2,793	147,84	40,173	10,95	5,586	-6,093	13,049	16,914	34,971	4,228	-2,327	-2,496
TMA0109-01c	1,97	113,94	45,326	7,573	4,868	-4,554	12,552	-19,68	31,161	4,328	-2,675	-3,366
TMA0109-01d	49,231	221,42	47,392	83,088	36,807	39,792	22,384	36,715	80,376	5,646	1,729	-1,598
TMA0109-01e	51,436	223,37	40,69	72,534	34,346	37,766	31,063	34,616	81,897	5,654	-3,164	1,111
TMA0109-01f	47,928	241,15	44,437	71,743	32,035	32,603	25,259	35,535	84,008	5,73	-2,342	-1,577
TMA0109-02a	2,816	176,68	89,891	19,726	5,966	5,097	1,126	-12,84	12,685	1,927	-2,631	1,621
TMA0109-02b	2,266	163,35	80,258	12,103	5,659	5,378	1,454	18,534	11,406	2,145	-2,718	1,269
TMA0109-02c	2,281	164,1	69,8	10,542	5,874	5,423	1,902	19,406	11,024	2,151	-2,269	-2,924
TMA0109-02d	32,609	210,82	69,524	72,206	36,596	38,413	9,014	25,279	49,693	5,785	-2,239	1,751
TMA0109-02e	31,787	206,17	56,291	68,494	36,346	39,853	12,411	37,189	49,155	6,064	-2,965	-3,812
TMA0109-02F	-5,468	-6,072	5,234	-3,114	9,684	-15	-12,01	-11,17	-22,06	18,616	-12,2	40,079
TMA0109-03A	-3,143	-3,47	2,041	-1,342	2,849	-7,619	-6,229	-6,432	-11,38	4,627	-8,291	4,83
TMA0109-03B	-3,758	-3,441	-2,306	-1,944	2,532	-7,917	-6,334	-5,998	-10,6	4,903	-8,248	4,332
TMA 0109-03c	-2,981	-3,583	-1,723	-1,762	3,82	-7,453	-6,192	-6,162	-11,12	4,861	-6,89	4,881
TMA0109-03D	-5,045	-5,565	-3,961	-4,492	6,359	-13,67	-12,85	-10,53	-20,95	9,222	-11,03	9,592
TMA0109-03E	-5,495	-5,908	-4,084	-4,248	4,743	-14,53	-12,96	-10,91	-21,04	6,859	-12,25	8,84
TMA0109-03F	-5,507	-6,201	-3,919	-4,207	5,592	-15,01	-12,43	-11,23	-20,84	9,196	-11,95	11,017
TMA0109-04a	3,169	-3,86	-3,158	-1,641	2,462	-8,406	-6,618	-8,337	-13,3	2,106	-8,046	-3,605
TMA0109-04B	-3,61	-3,982	-2,971	-2,215	-1,635	-8,896	-6,325	-7,153	-13	1,968	-7,066	-3,187
TMA0109-04C	-2,68	-4,15	-3,086	2,809	2,316	-8,807	-6,144	-6,459	-12,86	2,869	-8,236	-3,433
TMA0109-04d	-6,828	-6,816	-6,103	-4,705	2,254	-15,87	-13,54	-10,8	-22,43	4,362	-11,74	3,833
TMA0109-04 e	-6,921	-7,217	-6,866	-4,691	2,121	-17,7	-13,93	-12,6	-23,75	3,427	-13,62	-4,97
TMA0109-04 f	-6,453	-7,317	-5,611	-3,802	2,493	-15,84	-13,51	-12,44	-24,07	3,498	-12,29	-3,802
TMA0109-05A	-3,56	-4,332	-3,762	-1,896	-1,838	-8,803	-6,995	-6,7	-13,44	-0,921	-9,015	-3,922
TMA0109-05B	-3,065	-3,929	-3,553	-1,419	-1,965	-9,299	-6,342	-5,612	-12,67	-1,058	-9,724	-3,758
TMA0109-05C	-3,322	-4,409	-3,502	-2,19	1,543	-9,125	-7,266	-6,772	-13,57	0,679	-8,565	-3,608
TMA0109-05d	-5,523	-6,79	-6,133	-4,554	-2,79	-15,16	-13,5	-11,69	-22,16	0,979	-11,91	-5,303
TMA0109-05E	-5,718	-6,483	-6,502	-4,899	-3,388	-15,29	-13,62	-13,1	-22,87	1,044	-12,62	-5,5
TMA0109-05 f	-5,933	-6,517	-5,943	-3,932	-2,815	-15,61	-13,82	-11,62	-22,55	0,56	-12,71	-5,422
TMA1709-05c	92,563	6,24	7,608	18,288	-37,94	1423	-24,88	-10,53	-34,94	-7,22	-84,55	-77,57
TMA1709-05b	112,57	6,518	7,788	17,473	-40,49	2908,4	-24,74	-12,35	-35,56	-8,749	-84,78	-77,07
TMA1709-05a	94,73	5,721	7,465	17,714	-43,72	1782	-25,58	-14,06	-36,48	-9,364	-86,94	-77,82
TMA1709-04c	162,24	6,808	8,146	17,934	-35,15	1386,1	24,347	-9,404	-34,94	8,84	-85,22	-78,82
TMA1709-04b	120,51	5,797	8,123	18,732	-38,15	173,03	-23,06	-13,4	-33,83	-8,121	-83,47	-75,62
TMA1709-04a	79,76	6,87	9,286	19,425	-35,62	1260,1	25,448	-11,19	-34,86	8,404	-84,15	-78,24
TMA1709-03c	143,2	9,752	15,815	-24,15	-33,39	-99,58	-26,92	-25,94	-37,2	22,957	-96,15	-81,76
TMA1709-03b	113,18	10,168	16,695	-23,83	-30,91	1102,6	-27,33	-20,08	-37,35	23,825	-95,99	-80,87
TMA1709-03a	184,48	11,368	16,342	23,595	-32,34	1035,6	-27,75	-18,43	-36,89	34,5	-96,16	-81,26

TMA1709-02c	309,04	15,609	35,349	-29,39	28,348	799,64	-30,15	-31,78	-38,81	48,581	-99,31	-88,23
TMA1709-02b	212,85	17,518	36,668	-31,2	29,364	-99,76	-29,21	-31,8	-37,56	52,12	-99,16	-86,47
TMA1709-02a	118,77	18,921	37,888	-31,6	-26,72	Inf	-29,22	-29,83	-36,83	77,296	-99,05	-85,58
TMA1709-01c	-98,14	11,149	44,619	-24,52	22,822	1422	-41,74	-31,8	-48,11	245,87	148,56	-95,85
TMA1709-01b	589,22	10,196	40,328	-25,16	21,176	976,33	-42,26	-34,58	-48,29	140,76	132,91	-95,67
TMA1709-01a	Inf	12,223	45,16	-23,73	16,303	536,54	-41,57	-29,46	-47,02	167,91	222,28	-95,17
TMA2709-05c	-99,1	-13,52	-12,84	-25,44	-13,08	1235,7	-37,82	-44,75	-72,59	2,472	362,63	693,15
TMA2709-05b	-99,53	-13,29	-12,39	-29,64	17,048	1146	-39,19	-45,95	-71,52	-4,668	96,48	887,94
TMA2709-05a	-98,73	-13,72	-12,45	32,156	-11,58	1349	-38,35	-51,48	-72,23	-5,574	501,78	-99,99
TMA2709-04c	-99,53	-14,19	-12,38	-26,83	-11,6	1084,3	-38,29	-45,15	-73,25	12,083	329,26	895,23
TMA2709-04b	745,94	-13,01	-12,11	30,11	15,928	1145,2	-38,05	114,11	-71,11	16,419	374,67	-99,99
TMA2709-04a	1017,9	-13,03	-11,99	-22,92	-11,38	376,08	-38,24	84,083	-73,45	14,602	564,1	Inf
TMA2709-03c	-97,7	-14,4	-11,86	-27,83	10,577	780,59	-38,6	-42,42	-76,72	30,523	372,32	1857,1
TMA2709-03b	-98,61	-14,04	-10,96	-31,18	11,702	731,49	-38,49	-42,21	-75,01	35,424	181,18	787,08
TMA2709-03a	-98,19	-13,96	-11,2	-30,39	12,854	896,06	-40,16	-48,57	-76,33	40,926	639,31	876,26
TMA2709-02c	1916,1	-11,5	-8,267	46,401	16,463	1425,6	-35,79	83,083	-75,8	74,588	1334,6	Inf
TMA2709-02b	-98,41	-12,51	-7,664	-32,54	12,605	754,56	-36,66	-43,26	-76,16	89,342	363,94	602,76
TMA2709-02a	-98,47	-12,35	7,753	-26,62	17,318	573,6	-36,52	-41,42	-76,79	100,57	468,12	995,8
TMA2709-01b	-99,38	-13,43	12,28	-38,75	22,239	255	-38,01	-48,99	-80,7	174,17	-99,99	2747,6
TMA2709-01a	1368,6	-12,45	11,598	33,198	24,292	606,63	-37,19	92,759	-78,87	153,73	1013,3	-99,99
prop0208-01	-5,77	-5,722	-5,366	-4,719	-2,629	-15,37	-11,9	-9,934	-27,96	-1,504	-12,87	-2,788
prop0208-02	-5,06	-5,224	-5,242	-4,353	-2,32	-14,44	-11,94	-9	-27,09	0,805	-12,48	-2,809
prop0208-03	-5,154	-5,46	-5,299	-4,826	-3,64	-15,11	-12,09	-9,627	-26,81	-1,026	-13,82	-2,923
prop0208-04	-6,06	-5,802	-5,476	-4,964	-3,407	-15,09	-12,37	-9,56	-28,22	-1,038	-13,46	-3,194
prop0208-05	-7,441	-5,7	-5,682	-4,098	-3,374	-14,64	-11,69	-8,757	-26,46	-0,827	-12,76	-3,236
met1907-01	-3,569	-3,312	-3,207	-1,619	2,784	-10,58	-9,703	-7,345	-23,17	6,754	-11,59	3,08
met1907-02	4,989	-5,279	-5,183	-4,382	-2,286	-12,73	-12,03	-8,973	-25,39	1,478	-14,2	1,861
met1907-03	-4,807	-5,132	-5,219	-4,294	-2,479	-12,29	-11,91	-8,967	-24,49	-0,814	-13,88	-2,523
met1907-04	5,847	-5,228	-5,048	-4,598	-3,069	-12,75	-12,33	-8,884	-24,24	-1,019	-14,34	-3,263
eth2809-01a	-96,77	-13,97	-12,69	24,803	10,189	537,65	-38,69	42,295	-71,26	8,021	-99,58	568,86
eth2809-01b	-94,98	-12,54	-11,08	-22,03	-11,93	1298	-37,14	-41,52	-68,6	8,92	617,59	484,69
eth2809-01c	482,25	-12,18	-11,97	25,854	7,873	289,81	-36,91	115,18	-69,98	9,827	889,52	-99,98
eth2809-02a	490,68	-14,7	-13,5	-25,06	-9,958	262,46	-41,3	86,408	-73,36	6,541	1118,2	-99,99
eth2809-02b	-98,13	-12,93	-12,83	58,012	12,707	-74,78	-39,37	253,59	-70,84	6,759	1365,8	-99,99
eth2809-02c	-95,93	-12,52	-13,28	-28,91	-17,03	1306,1	-38,33	43,512	-70,02	5,924	404,01	477,72
eth2809-03a	-95,97	-14,25	-13,29	26,373	9,79	749,14	-40,15	164,5	-74,47	5,422	-99,66	539,6
eth2809-03b	-95,86	-13,61	-13,29	-33,58	11,107	530,94	-39,53	57,483	-71,85	4,185	603,62	536,64
eth2809-03c	-98,14	-14,01	-13,28	-27,19	17,888	2186,8	-38,69	42,68	-71,74	4,714	-99,73	506,43
eth2809-04a	-96,48	-12,25	-12,18	-25,11	13,31	788,21	-38,25	54,304	-71,31	3,476	603,62	-99,99
eth2809-04b	696,94	-11,62	-10,97	61,947	20,352	343,06	-37,99	159,76	-68,28	-5,211	780,8	-99,99
eth2809-04c	-97,37	-11,22	-11,62	42,223	18,704	2082,6	-37,09	126,08	-68,57	7,383	1620,8	-99,99

eth2809-05a	854,43	-8,646	-10,78	-26,25	9,728	673,1	-34,05	58,661	-66,51	6,318	1334,6	905,66
eth2809-05b	1041,1	-11,37	-10,96	36,888	-10,45	142,64	-35,77	95,006	-68,46	6,038	1748,3	1614,2
eth2809-05c	-99,27	-12,27	-11,72	50,206	-15,07	818,65	-35,98	-41,26	-67,48	-6,907	-99,79	-99,99
eth2408-01a	70,977	4,828	150,17	102,88	7,571	84,789	5,41	39,544	22,041	2,78	1,195	2,539
eth2408-01b	74,602	4,949	131,72	107,24	7,237	83,138	5,979	45,885	20,629	2,302	-1,47	-2,789
eth2408-01c	72,04	4,525	116,9	109,4	7,734	84,044	4,948	41,518	18,105	2,61	-1,217	2,695
eth2408-02a	62,154	4,041	183,37	113,92	7,182	84,51	4,478	60,378	22,998	3,02	-3,031	-3,714
eth2408-02b	68,461	4,459	146,93	112,12	7,895	85,25	5,012	49,92	22,769	2,418	1,255	1,958
eth2408-02c	70,123	4,317	161,3	105,3	7,222	85,604	5,64	49,714	17,733	2,821	-2,358	1,946
eth2408-03a	56,065	4,14	187,03	111,5	6,981	84,117	4,93	64,983	24,952	3,132	1,546	1,24
eth2408-03b	55,977	3,651	192,87	114,88	7,156	82,998	4,182	61,362	24,489	2,821	1,502	-2,454
eth2408-03c	56,468	3,827	176,4	110,58	6,984	82,072	5,401	67,261	21,789	3,482	-3,455	-2,623
eth2408-04a	31,061	3,416	218,91	100,99	5,835	75,395	4,117	75,43	29,603	3,237	-3,416	1,568
eth2408-04b	35,287	3,424	204,3	97,462	6,355	78,919	4,717	73,313	26,593	3,575	-2,136	-2,745
eth2408-04c	37,552	4,063	202,76	102,08	6,369	79,56	4,235	66,393	25,142	2,893	1,698	-2,694
eth2408-05a	13,564	2,864	208,97	68,421	3,729	50,038	4,003	92,433	32,706	3,61	1,391	-2,679
eth2408-05b	16,117	2,749	198,42	76,4	4,282	55,329	3,986	85,362	28,889	3,554	1,153	-2,309
eth2408-05c	20,48	3,521	202,15	89,965	4,987	65,814	5,022	80,237	28,994	3,574	1,565	1,821
bút2807-02	-4,817	-5,304	-6,063	-5,133	-2,151	-16,27	-13,5	-8,864	-27,11	-1,823	-14,03	-3,425
bút2807-03	-4,579	-4,962	-5,207	-4,691	-2,36	-13,77	-12,77	-8,539	-25,3	-1,177	-13,51	-3,135
bút2807-04	-6,104	-4,834	-5,271	-6,002	-3,209	-12,55	-12,63	-9,589	-21,73	-2,048	-14,41	-3,23
bút2807-05	-5,687	-4,643	-4,932	-4,795	-2,683	-12,07	-12,51	-9,429	-19,01	-2,072	-14,29	-3,753
o-isoam-01 0308	-6,671	-5,407	-5,367	-5,008	-3,509	-14,28	-12,39	-8,738	-26,93	-2,613	-12,61	-2,896
o-isoam-02 0308	-5,471	-5,486	-5,475	-4,425	-2,968	-14,07	-12,44	-9,639	-26,65	-2,292	-12,95	-2,634
o-isoam-03 0308	-5,16	-4,525	-4,891	-4,016	-2,858	-12,5	-11,45	-7,608	-25,98	-0,67	-11,58	-2,736
o-isoam-04 0308	-5,884	-4,881	-4,967	-4,456	-3,023	-12,89	-11,32	-7,121	-25,47	0,787	-12,51	-2,403
o-isoam-05 0308	5,143	-4,27	-4,476	-4,064	-2,589	-11,27	-10,63	-6,581	-23,22	-1,058	-12,03	-2,456

Divergence data for measurements of salted fish samples with BH 213 unit

	1/Div.	2/Div.	3/Div.	4/Div.	5/Div.	6/Div.	7/Div.	8/Div.	9/Div.	10/Div.	11/Div.	12/Div.
o-saltf4666-160999c	10,395	6,845	5,34	23,45	27,081	65,845	32,736	-27,78	-24,48	1,478	-45,41	-63,01
o-saltf4666-160999b	5,685	6,967	5,441	22,601	29,692	73,477	33,608	-29,91	-24,26	-2,37	-48,02	-61,02
o-saltf4666-160999a	10,88	6,841	5,357	22,91	29,833	80,796	32,901	-30,23	-25,11	-2,763	-54,14	-60,62
o-saltf4665-1509c	9,339	6,093	3,804	12,457	7,818	237,05	33,825	-11,12	-21,37	-0,978	-36,19	-2,522
o-saltf4665-1509b	7,064	5,953	4,688	12,917	8,931	318,49	36,378	11,892	-20,92	-1,725	-37,3	-2,63
o-saltf4665-1509a	9,453	6,013	5,328	15,53	9,346	321,52	37,686	11,279	-20,39	1,109	-39,24	-3,135
o-saltf4663-1509c	5,681	6,359	5,792	9,047	7,481	7,535	35,374	11,565	-25,39	-1,64	-60,4	-3,611
o-saltf4663-1509b	5,798	6,428	5,786	9,032	7,504	8,235	36,289	-12,15	-26,2	1,606	-59,87	-4,022
o-saltf4663-1509a	6,294	6,379	5,466	9,835	7,043	7,302	35,89	12,434	-26,49	3,814	-62,42	-4,008
o-saltf4570-1509c	1,876	5,387	3,982	-3,017	5,698	6,595	4,605	5,387	25,309	-2,418	-9,026	3,065
o-saltf4570-1509b	2,215	5,892	3,957	-1,279	6,89	6,818	4,302	3,71	24,183	2,149	-8,57	2,425
o-saltf4570-1509a	2,696	5,691	3,953	2,098	6,895	6,85	4,815	-3,094	24,418	3,143	-9,466	2,314
o-saltf4569-1509f	4,814	6,617	6,435	9,292	7,776	8,006	36,766	11,882	-27,71	-2,956	-61,55	-4,371
o-saltf4569-1509e	4,844	5,996	5,835	8,26	7,157	8,207	35,57	11,695	-27,4	-4,244	-63,35	-4,722
o-saltf4569-1509d	4,356	5,661	5,933	8,108	7,743	7,699	37,513	11,823	-28,3	-3,751	-60,48	-4,8
o-saltf4569-1509c	5,225	6,749	6,861	8,187	7,634	7,609	39,77	13,231	-27,35	-5,958	-56,59	-4,872
o-saltf4569-1509b	5,312	6,636	6,209	7,754	7,815	7,704	38,284	12,234	-27,63	-6,197	-59,64	-4,821
o-saltf4353-1509c	1,997	6,597	4,748	-2,711	7,274	7,295	5,403	6,551	26,238	3,115	-10,12	3,325
o-saltf4353-1509b	2,691	6,964	4,539	1,913	7,311	7,013	5,816	7,862	27,258	2,898	-9,733	3,643
o-saltf4353-1509a	2,588	6,061	3,898	1,749	6,757	6,606	5,277	5,716	26,248	2,191	-9,92	3,578
o-saltf2-4666-1609f	31,862	7,711	5,059	27,626	15,733	2404,1	36,988	-9,102	-22,88	1,293	-47,72	175,47
o-saltf2-4666-1609e	29,763	7,534	5,175	28,894	12,905	2461,1	35,616	-9,888	-23,18	-0,979	-43,96	153,67
o-saltf2-4666-1609d	19,191	8,866	5,56	27,276	16,927	664,46	35,541	-10,33	-20,86	-1,076	53,858	185,42
o-saltf2-4666-1609c	9,683	11,715	4,675	26,271	16,605	242,14	43,104	-4,275	18,915	1,573	82,889	225,15
o-saltf2-4666-1609b	11,795	11,224	5,093	28,162	16,926	672,57	41,498	-5,183	17,989	-1,581	46,051	233,96
o-saltf2-4666-1609a	7,181	11,464	5,386	26,091	15,945	233,11	39,05	-3,256	19,14	-1,551	31,013	211,99
o-saltf2-4353-1609c	92,461	7,507	7,122	32,452	13,773	1145,2	33,362	3,982	15,073	1,045	91,497	167,14
o-saltf2-4353-1609b	66,008	7,047	6,996	27,755	9,059	586,31	32,752	2,951	15,433	-1,566	41,495	175,13
o-saltf2-4353-1609a	52,351	7,345	6,482	26,394	11,788	-98,91	33,133	-3,953	16,444	-0,854	44,173	167,84

saltf2=salted fish whole filletts in plastic bags 4353 (mgN 90) , (advanced spoilage) and 4666 (mgN 35,4)
saltf=salted fish chopped and mixed samples 4353 (mgN90), 4666 (mgN35,4), 4663 (mgN31,3), 4570 (mgN20), 4665 (mgN34,2), 4569 (mgN16) .

Divergence data for measurements of salmon, fishmeal and salted fish samples with BH 213 unit

	1/Div.	2/Div.	3/Div.	4/Div.	5/Div.	6/Div.	7/Div.	8/Div.	9/Div.	10/Div.	11/Div.	12/Div.
lax0809a	2,419	3,162	3,034	-2,697	4,924	5,093	8,178	3,888	7,684	-2,752	-8,74	2,233
lax0809b	2,275	3,206	3,131	2,319	4,97	4,708	7,544	3,004	-4,889	-2,348	-6,426	1,337
lax0809c	-2,511	2,69	3,422	-3,823	5,138	5,59	6,169	5,099	7,064	-2,151	-7,179	2,472
laxput0809a	2,658	5,642	3,216	5,404	6,15	6,194	7,264	5,265	15,107	2,257	-7,012	2,094
laxput0809b	-2,262	5,032	3,274	6,511	6,428	6,324	6,097	4,079	15,083	2,539	-7,499	1,967
laxput0809c	2,163	5,43	3,413	5,913	6,041	6,035	4,833	4,226	13,507	2,087	-8,156	-1,868
old síldar A	3,161	1,35	2,569	1,27	4,417	4,416	1,902	-2,054	2,422	2,279	-3,492	3,765
old síldar B	2,709	0,991	2,443	1,551	2,871	4,179	1,522	2,148	2,066	2,171	1,989	3,41
old síldar C	2,469	1,387	2,402	1,53	4	4,135	1,158	-2,688	1,802	2,543	2,131	3,493
old síldar D	3,387	1,937	3,134	2,178	4,038	5,392	2,563	-2,739	3,997	2,607	-2,206	3,993
4570c	1,876	5,387	3,982	-3,017	5,698	6,595	4,605	5,387	25,309	-2,418	-9,026	3,065
4570b	2,215	5,892	3,957	-1,279	6,89	6,818	4,302	3,71	24,183	2,149	-8,57	2,425
4570a	2,696	5,691	3,953	2,098	6,895	6,85	4,815	-3,094	24,418	3,143	-9,466	2,314
4353c	1,997	6,597	4,748	-2,711	7,274	7,295	5,403	6,551	26,238	3,115	-10,12	3,325
4353b	2,691	6,964	4,539	1,913	7,311	7,013	5,816	7,862	27,258	2,898	-9,733	3,643
4353a	2,588	6,061	3,898	1,749	6,757	6,606	5,277	5,716	26,248	2,191	-9,92	3,578

Divergence data for measurements of water with DLC unit

	1/Div.	2/Div.	3/Div.	4/Div.	5/Div.	6/Div.	7/Div.	8/Div.	9/Div.	10/Div.	11/Div.	12/Div.
water0824	9,656	-2,615	179,03	50,87	3,267	38,004	4,328	101,7	37,185	4,036	-2,533	1,572
water0820a	77,326	19,02	49,572	54,78	14,958	81,604	5,672	50,342	15,536	2,642	-1,902	1,415
water0820b	65,725	6,21	136	118,4	11,077	90,787	6,535	49,95	19,861	3,474	-3,151	-3,251
water0820c	71,754	7,563	98,561	125,36	12,346	87,95	6,5	43,619	16,406	2,988	-2,556	-2,568
watin3108a	55,81	75,029	210,28	74,723	38,69	65,001	6,352	30,496	25,2	3,634	-2,469	-3,796
watin3108b	33,99	197,71	96,069	50,067	31,959	39,803	4,525	-21,72	11,168	1,98	-1,95	-2,912
watin3108c	32,223	201,58	87,851	38,762	31,699	38,412	4,507	-27,3	9,993	2,33	-2,956	2,285
wbetw3108a	12,909	235,37	23,308	-16,26	21,082	24,5	3,623	20,322	8,486	2,031	2,24	-2,547
wbetw3108b	20,134	253,98	20,115	25,856	29,369	33,346	8,589	25,856	13,367	6,942	7,633	6,586
wbetw3108c	13,147	259,52	22,971	26,494	20,952	21,673	3,112	-18,95	11,053	2,043	-2,73	-3,559
watend3108a	15,911	242,1	24,331	29,366	23,249	26,629	3,563	-19,66	10,883	1,734	-2,253	-2,87
watend3108b	17,043	240,67	26,056	21,484	24,177	27,465	3,301	-18,21	11,078	2,14	-2,909	-3,452
watend3108c	14,088	237,64	18,948	30,091	22,773	28,06	3,597	19,407	11,133	1,845	-2,468	-2,882
wend3108d	11,546	255,74	-18,7	34,961	21,29	22,579	3,875	-19,74	11,42	1,664	-3,455	-3,142

Divergence data for measurements of standards with DLC unit

n-TMA0109-01d	49,231	221,42	47,392	83,088	36,807	39,792	22,384	36,715	80,376	5,646	1,729	-1,598
n-TMA0109-01e	51,436	223,37	40,69	72,534	34,346	37,766	31,063	34,616	81,897	5,654	-3,164	1,111
n-TMA0109-01f	47,928	241,15	44,437	71,743	32,035	32,603	25,259	35,535	84,008	5,73	-2,342	-1,577
n-TMA0109-02d	32,609	210,82	69,524	72,206	36,596	38,413	9,014	25,279	49,693	5,785	-2,239	1,751
n-TMA0109-02e	31,787	206,17	56,291	68,494	36,346	39,853	12,411	37,189	49,155	6,064	-2,965	-3,812
n-TMA0109-02f	26,679	218,27	55,11	51,421	34,279	38,001	14,702	26,192	53,305	5,541	2,075	1,531
n-TMA0109-03a	42,459	167,1	53,43	81,108	41,275	49,11	4,988	24,382	13,523	2,524	2,451	-2,392
n-TMA0109-03b	41,97	180,46	173,84	60,917	40,72	49,503	4,284	20,626	16,055	3,15	2,375	-3,016
n-TMA0109-03c	38,637	189,03	531,42	60,209	39,879	48,059	5,407	21,497	19,909	3,589	1,86	1,267
n-TMA0109-04a	49,944	166,32	15,617	65,011	42,914	56,779	4,905	23,848	10,085	2,102	2,605	-3,523
n-TMA0109-04b	47,368	176,93	25,298	65,949	41,32	53,85	5,358	28,769	13,139	2,127	2,07	-2,659
n-TMA0109-04c	46,732	181,3	25,176	60,948	41,74	51,424	5,052	-16,24	10,306	1,496	2,126	-3,222
n-TMA0109-05a	69,505	14,587	115,36	121,38	21,081	84,053	5,39	22,122	11,959	2,856	-0,995	2,347
n-TMA0109-05b	68,271	18,547	102,07	112,81	22,789	78,845	5,4	16,013	9,694	1,72	-1,365	4,342
n-TMA0109-05c	63,948	34,99	63,608	100,21	30,187	70,123	5,19	-18,7	7,739	1,226	1,177	3,635
n eth0824-01A	70,977	4,828	150,17	102,88	7,571	84,789	5,41	39,544	22,041	2,78	1,195	2,539
n eth0824-01B	74,602	4,949	131,72	107,24	7,237	83,138	5,979	45,885	20,629	2,302	-1,47	-2,789
n eth0824-01C	72,04	4,525	116,9	109,4	7,734	84,044	4,948	41,518	18,105	2,61	-1,217	2,695
n eth0824-02A	62,154	4,041	183,37	113,92	7,182	84,51	4,478	60,378	22,998	3,02	-3,031	-3,714
n eth0824-02B	68,461	4,459	146,93	112,12	7,895	85,25	5,012	49,92	22,769	2,418	1,255	1,958
n eth0824-02C	70,123	4,317	161,3	105,3	7,222	85,604	5,64	49,714	17,733	2,821	-2,358	1,946
n eth0824-03A	56,065	4,14	187,03	111,5	6,981	84,117	4,93	64,983	24,952	3,132	1,546	1,24
n eth0824-03B	55,977	3,651	192,87	114,88	7,156	82,998	4,182	61,362	24,489	2,821	1,502	-2,454
n eth0824-03C	56,468	3,827	176,4	110,58	6,984	82,072	5,401	67,261	21,789	3,482	-3,455	-2,623
n eth0824-04A	31,061	3,416	218,91	100,99	5,835	75,395	4,117	75,43	29,603	3,237	-3,416	1,568
n eth0824-04B	35,287	3,424	204,3	97,462	6,355	78,919	4,717	73,313	26,593	3,575	-2,136	-2,745
n eth0824-04C	37,552	4,063	202,76	102,08	6,369	79,56	4,235	66,393	25,142	2,893	1,698	-2,694
n eth0824-05A	13,564	2,864	208,97	68,421	3,729	50,038	4,003	92,433	32,706	3,61	1,391	-2,679
n eth0824-05B	16,117	2,749	198,42	76,4	4,282	55,329	3,986	85,362	28,889	3,554	1,153	-2,309
n eth0824-05C	20,48	3,521	202,15	89,965	4,987	65,814	5,022	80,237	28,994	3,574	1,565	1,821
n-meth0824-01A	67,416	15,255	51,84	106,71	20,222	74,658	5,529	33,154	16,656	2,298	-0,901	2,937
n-meth0824-01B	64,695	18,606	35,59	94,025	23,433	79,717	6,998	62,474	13,773	3,271	-1,146	-3,485
n-meth0824-01C	61,339	23,061	26,949	100,71	24,253	70,078	5,599	28,046	15,292	2,028	-0,925	3,54
n-meth 0824-02A	58,829	4,915	275,49	136,05	9,96	86,792	5,075	32,952	16,653	2,507	-1,586	4,247
n-meth0824-02B	69,938	7,045	210,81	131,38	12,079	89,801	4,647	34,537	13,76	2,845	1,247	3,135
n-meth0824-02C	74,524	7,416	193,76	130,13	13,243	90,922	5,275	32,325	20,881	2,474	-1,121	4,328
n-meth0824-03A	68,355	12,898	43,588	100,12	17,88	80,505	6,229	72,568	15,214	2,975	-2,014	-2,714
n-meth0824-03B	63,066	10,674	54,824	103,78	15,245	77,224	5,697	24,229	17,541	2,056	-1,606	4,066
n-meth0824-04A	66,951	5,207	182,81	112,7	8,918	88,385	5,406	49,701	18,275	3,017	-2,077	2,399
n-meth0824-04B	73,416	6,805	130,65	105,42	11,171	87,919	5,797	35,729	13,078	2,563	-2,346	-2,5
n-meth0824-04C	72,264	7,2	121,57	118,84	12,033	86,565	5,378	33,623	17,837	2,429	1,049	2,966
n-meth0824-05A	45,058	4,397	273,51	122,4	7,507	85,509	4,772	44,483	19,887	2,709	1,168	3,067
n-meth0824-05B	54,837	4,819	220,68	113,94	8,276	87,069	5,291	40,799	21,721	2,623	-1,781	-2,396
n-meth0824-05C	20,48	3,521	202,15	89,965	4,987	65,814	5,022	80,237	28,994	3,574	1,565	1,821

Divergence data for measurements of salted fish and fishmeal with DLC unit

	1/Div.	2/Div.	3/Div.	4/Div.	5/Div.	6/Div.	7/Div.	8/Div.	9/Div.	10/Div.	11/Div.	12/Div.
n-saltf4570-1409a	4,746	219,86	-15,7	-15,42	15,655	13,929	2,235	20,458	8,197	-1,692	-1,809	-2,662
n-saltf4570-1409b	4,462	221,84	-15,43	12,231	15,749	13,853	2,094	26,608	7,064	-1,441	2,158	-3,127
saltf4570-1409c	3,594	226,12	-18,43	-16,09	14,323	11,42	1,909	18,89	7,762	1,474	-2,73	-3,434
saltf4353-1409a	-2,142	217,34	-19,42	-9,092	8,503	7,071	1,48	21,369	-8,994	1,397	2,524	-3,192
saltf4353-1409b	-2,373	224,8	-19,93	-9,844	8,922	6,882	1,542	21,42	8,621	1,432	2,365	-2,954
saltf4353-1409c	-2,696	220,93	-20,84	-9,824	10,829	8,186	1,435	24,026	8,259	-1,466	2,143	-3,589
n-síld3108A	-2,437	-22,41	-13,82	-5,847	-13,36	-7,021	1,398	36,373	-6,941	2,158	0,843	-1,799
n-síld3108B	-2,56	-10,02	9,249	-7,756	-0,822	1,37	-0,686	-10,31	-6,083	0,86	1,514	2,024
n-síld3108C	-2,444	-5,98	-10,99	7,961	-1,889	-5,003	0,671	-18,06	-6,487	1,172	-2,056	-3,257
n-síld3108D	-1,152	-17,39	12,989	10,989	-1,619	-2,336	0,705	19,136	5,78	1,348	-1,954	-3,574
n-síld3108E	1,977	-7,53	13,055	7,633	-3,191	-4,401	-1,375	-26,21	-5,405	-1,914	-2,066	1,967

Divergence data for measurements of haddock fillets with BH 213 unit

	1/Div.	2/Div.	3/Div.	4/Div.	5/Div.	6/Div.	7/Div.	8/Div.	9/Div.	10/Div.	11/Div.	12/Div.
o-hadfil2709l	-99,54	-15,82	-15,1	-38,53	-15,45	820,22	-46,47	-74,39	-81,08	-11	515,64	618,23
o-hadfil2709i	-99,59	-14,78	-15,08	-37,51	-19,72	3237,9	-45,31	90,399	-81,74	-11,79	1245,5	-99,99
o-hadfil2709h	737,25	-15,19	-14,98	-41,12	21,656	1016,8	-45,16	-69,25	-82,91	-9,893	566,14	Inf
o-hadfil2709g	-99,44	-15,38	-14,42	-41,34	-15,29	1649,8	-44,3	-68,52	-82,53	-13,31	149,31	-99,99
o-hadfil2709f	2136,9	-14,61	-15,04	61,53	16,818	304,69	-43,61	-71,12	-84,13	-13,34	4945,1	737,25
o-hadfil2709e	-99,53	-15,52	-14,97	-42,91	16,193	833,35	-46,41	-81,55	-86,17	-16,25	575,78	-99,99
o-hadfil2709d	641,38	-12,83	-11,61	-40,36	-11,04	910,26	-34,17	-54,87	-78,35	-14,83	672,48	-99,09
o-hadfil2709c	641,38	-12,83	-11,61	-40,36	-11,04	910,26	-34,17	-54,87	-78,35	-14,83	672,48	-99,09
o-hadfil2709b	1728,4	-10,41	-10,39	-31,46	12,097	626,66	-32,15	60,137	-76,85	17,702	2028,2	-98,37
o-hadfil2709a	-99,54	-10,68	-10,05	-35,77	-18,87	1447,9	-29,26	-73,29	-76,28	-20,38	-99,98	-91,67
o-hadfil2909a	-95,36	-10,88	-11,11	-32,19	-13,78	597,05	-38,71	140,77	-68,44	-7,307	143,68	-98,14
o-hadfil2909b	427,45	-9,793	-10,76	30,23	15,188	-66,81	-37,52	74,263	-66,44	5,977	348,88	-98,11
o-hadfil2909c	-90,92	-10,29	-10,25	-26,15	-9,05	295,41	-35,51	-44,73	-63,6	-3,93	-94,91	-98,56
o-hadfil2909d	-92,24	-10,79	-11,11	-32,8	-11,04	713,33	-38,12	-52,23	-64,2	-5,441	147,84	-98,49
o-hadfil2909e	538,32	-10,94	-11,25	-26,63	-11,04	111,74	-39,24	85,622	-64,31	-4,472	292,72	-98,64
o-hadfil0110a	-95,35	-8,902	-8,322	-16,88	-14,95	920,69	-25,03	-58,72	-47,48	7,01	271,5	1030,2
o-hadfil0110b	256,61	-10,22	-8,723	21,172	12,323	168,67	-28,12	153,54	-52,46	-4,825	381,47	437,55
o-hadfil0110c	-91,03	-9,943	-9,433	-20,03	-14,39	359,41	-31	150,21	-54,78	-4,43	348,05	735,24
o-hadfil0610a	-92,16	-6,277	-6,82	-37,17	-39,16	285,05	-16,6	82,495	43,341	-19,22	108,12	89,197
o-hadfil0610b	-89,52	-6,063	-7,198	-28,67	-37,88	214,17	-24,81	-68,87	-55,93	-18,7	-87,71	131,77
o-hadfil0610c	342,94	-6,719	-7,716	-23,35	-21,71	181,26	-29,36	86,164	-58,75	-13,48	-88,98	206,52
o-hadfil0610d	-85,34	-7,652	-8,387	-30,74	-23,44	437,44	-32,41	-57,97	-59,56	-14,37	-90,84	245,7
o-hadfil0610e	-87,12	-8,842	-9,517	-25,82	-15,52	438,65	-33,86	-52,86	-59,33	-11,31	120,22	340,25
o-hadfil0610f	-91,86	-9,994	-10,76	-27,43	-15,98	469,5	-37,28	-51,8	-61,27	-12,34	-93,91	218,83
o-hadfil0810a	-87,31	-15,64	-15,91	-29,95	-26,68	191	-53,35	513,1	-83,5	12,909	291,06	178,11
o-hadfil0810b	365,42	-16,88	-17,18	-35,02	-14,1	238,54	-51,19	1289,2	-82,92	12,4	259,71	242,18
o-hadfil0810c	-93,02	-17,92	-17,3	-33,45	-15,6	468,05	-51,43	139,68	-82,64	-16,62	-99,21	827,32
o-hadfil1110a	-90,86	-12,61	-13,02	-28,15	12,634	433,23	-41,67	101,63	-75,98	-4,557	239,88	195,29
o-hadfil1110b	243,14	-14,3	-12,24	-26,33	23,819	229,51	-41,72	141,73	-76,2	3,978	-98,07	243,14
o-hadfil1110c	-88,41	-13,57	-12,66	-25,97	16,177	177,71	-41,69	153,05	-76,58	8,663	330,68	-99,95
o-hadfil1110d	128,93	-13,43	-13,54	-34,46	-11,56	933,54	-43,47	100,6	-76,85	-6,759	-98,45	188,19

Divergence data for measurements of standard samples with new BH 213 unit-DLC

	1/Div.	2/Div.	3/Div.	4/Div.	5/Div.	6/Div.	7/Div.	8/Div.	9/Div.	10/Div.	11/Div.	12/Div.
et-50a	-99,4	-99,42	-99,41	-99,4	-99,42	-99,36	-99,36	-99,4	-99,37	-99,42	-99,35	-99,33
et-50b	88,48	92,95	95,119	95,082	91,133	87,215	92,91	79,788	94,197	41,75	97,301	83,174
et-50c	74,332	87,387	82,907	83,988	80,622	76,484	82,479	62,587	81,525	33,871	84,786	73,992
et-100a	76,304	84,026	81,151	84,124	81,005	76,581	83,227	60,52	81,102	33,95	83,927	74,291
et-100b	78,08	81,042	84,194	84,27	79,942	76,391	82,361	59,947	81,666	33,096	86,927	73,294
et-100c	78,08	81,042	84,194	84,27	79,942	76,391	82,361	59,947	81,666	33,096	86,927	73,294
et-200a	80,507	83,542	84,258	84,409	81,27	77,175	82,428	58,99	82,439	38,335	86,091	75,347
et-200b	77,74	80,661	82,657	83,553	79,926	76,545	82,716	58,541	81,121	38,278	85,59	75,766
et-200c	54,73	76,786	58,021	78,48	66,036	70,368	72,002	48,321	79,504	29,256	82,087	69,712
et-500a	72,506	79,185	78,959	69,728	72,468	70,301	77,268	57,442	78,16	27,58	74,789	70,004
et-500b	92,748	99,647	102,19	89,899	91,099	89,462	97,344	74,642	100,64	42,433	94,633	89,344
et-500c	75,267	78,745	80,85	71,529	71,773	70,746	77,929	57,009	79,976	28,932	76,469	70,086
et-1000a	75,16	81,32	82,436	70,788	73,661	71,498	78,276	56,236	79,782	33,431	75,097	70,824
et-1000b	76,328	82,898	82,49	71,064	73,326	70,675	77,935	55,205	79,165	28,561	75,981	70,679
et-1000c	73,302	83,782	80,791	70,982	73,804	71,061	78,683	55,162	78,102	28,758	75,035	70,876
et-2000a	75,748	81,28	82,597	71,033	73,022	71,602	78,396	56,091	78,687	28,734	75,916	70,52
et-2000b	76,292	81,12	81,73	70,753	72,741	70,723	78,677	54,92	77,566	28,742	75,451	72,297
et-2000c	74,766	83,097	80,334	71,173	74,399	70,756	78,897	54,336	77,54	28,491	74,937	70,997
wat-2302b	72,657	80,508	76,148	70,96	70,826	70,213	78,263	57,009	76,573	25,326	76,101	70,211
wat-2302c	65,17	80,281	76,501	68,608	71,291	69,62	77,759	57,266	79,426	43,956	74,481	77,708
wat-2402a	75,779	75,811	84,776	82,805	80,457	76,507	81,796	56,441	80,417	30,938	85,471	73,66
wat-2402b	78,446	92,301	85,785	86,182	80,845	75,775	82,993	76,271	82,822	40,95	86,64	73,772
wat-2402c	-99,54	-99,52	-99,49	-99,58	-99,66	-99,67	-91,76	72,989	86,736	61,372	85,877	85,619
wat-2502a	82,971	91,746	86,61	94,909	85,117	81,598	84,09	76,019	83,602	36,437	89,742	74,944
wat-2502b	82,38	90,634	85,661	91,104	84,956	81,965	83,581	70,625	83,161	34,724	88,333	74,257
wat-2502c	79,825	88,991	86,214	89,874	85,409	81,862	83,291	65,914	81,378	35,128	90,497	74,032
TMA100a	71,105	80,304	79,094	88,557	81,686	79,639	82,141	62,212	82,418	34,618	87,964	72,883
TMA100b	81,564	83,555	82,498	89,721	83,928	81,086	83,894	59,176	81,746	33,735	87,911	74,396
TMA100c	-99,49	-99,54	-99,64	-99,64	-99,63	-99,65	-91,43	60,847	82,453	61,84	89,436	84,74
TMA300a	75,603	83,791	82,408	89,377	84,063	80,759	83,011	59,5	81,962	34,696	89,199	74,625
TMA300b	77,804	80,879	85,261	88,945	84,776	80,712	82,056	58,072	81,421	32,892	88,858	71,867
TMA300c	80,122	84,578	84,221	89,185	83,539	82,226	81,956	57,302	82,064	52,352	88,493	77,503

Appendix 2

Presentation at Nordic Sensory Workshop VIII

G. Olafsdóttir, Electronic Nose Instead of Sensory Analysis?
Sensory Evaluation and Quality, Nordic Sensory Workshop VIII,
Reykjavík, Iceland, September 9-11, 1999

Sensory Evaluation and Quality, Workshop VIII,

Reykjavík, Iceland, September 9-11, 1999

Electronic Nose Instead of Sensory Analysis?

G. Olafsdóttir, Icelandic Fisheries Laboratories, e-mail gudrun@rfisk.is, http://www.rfisk.is

ELECTRONIC NOSE INSTEAD OF SENSORY ANALYSIS ?

Gudrun Ólafsdóttir
Rf - Icelandic Fisheries Laboratories, P.O. Box 1405,
121 Reykjavík, Iceland
Tel. 354 562 0240, Fax 354 5620740, E-mail: gudrun@rfisk.is
http://www.rfisk.is

G.Ó./1999

Summary

- Electronic nose development
- Electronic nose - a rapid technique to evaluate fish freshness
  - Development of the electronic nose FreshSense in Iceland for fish freshness evaluation
  - "Electronic Profiling of Food and Bevarage Odour for Quality Determinations" (FAIR CT98 3436) - using the electronic nose Bloodhound for fish products
- Future prospects for Electronic Nose

G.Ó./1999

Electronic Nose development

- 1980´s first introduction of the concept EN
  - array of gas sensors
  - mimic the human sense of smell
- 1991 first EN conference in Reykjavík, Iceland
  - UK, Germany, France, Sweden, Canada, USA
- 1990´s active research on different sensor technologies and launching of EN instruments
- 1999 NOSE - Network on Artificial Olfactory Sensing - EU project - http://nose.uia.ac.be/

G.Ó./1999

Electronic Nose manufacturers

Alpha M.O.S multi organoleptic systems

ORIGO

Bloodhound

NST NORDIC SENSOR TECHNOLOGIES

AROMA SCAN

CYRANO Sciences, Inc.

lennartz electronic
Lennartz electronic GmbH
Bismarckstrasse 136
D-72072 Tübingen
Bundesrepublik Deutschland / Federal Republic of Germany
Tel. / Phone: +49-(0)7071-93550
Fax: +49-(0)7071-935530
Email: info@lennartz-electronic.de
Web: www.lennartz-electronic.de

G.Ó./1999

Requirements for EN in industry and in research laboratories

Sensors

- Selective and sensitive for different volatile compounds
- minimal long term drift
- recovery time short
- reproducible

EN instruments

- robust and able to withstand conditions in industry
- laboratory EN instruments v.s. classical analytical instruments
- easy operation and user friendly software
- fast analysis time (< 2 minutes)
- standardised measurement and calibration routines necessary

Correlation of the output from EN instrument to a reference method (i.e. sensory evaluation) is necessary for each application

G.Ó./1999

Various sensor technologies in EN´s

- ☑ Semiconducting Metal Oxide Sensors (MOS)
- ☑ Metal Oxide Field Effect Transistors (MOSFET)
- ☑ Surface Acoustic Wave sensors (SAW)
- ☑ Quarts Microbalance sensors (QMB)
- ☑ Electrochemical sensors
- ☑ Infrared sensors
- ☑ Discotic Liquid Crystal sensors (DLC)
- ☑ Polyconducting polymer sensors
- ☑ Quadrupole technology as a mass sensor

G.Ó./1999

Sensory Evaluation and Quality, Workshop VIII,

Reykjavík, Iceland, September 9-11, 1999

Electronic Nose Instead of Sensory Analysis?

G. Olafsdóttir, Icelandic Fisheries Laboratories, e-mail gudrun@rfisk.is, http://www.rfisk.is

Sampling procedures for EN

- Static headspace sampling
  - sample preparation minimal
- Dynamic sampling
  - dynamic bubling
  - purge and trap

- long equilibration time for volatile compounds
- temperature monitoring during sampling
  - 0°C - 25°C or heated 35- 70°C
- weight of sample v.s. surface area
- optimisation of sampling procedures for different products
- standardisation of sampling procedures

Data analysis for EN

- Links to Excel
  - study characteristic sensor responses
  - optional data handling (slope, final value, area, base line value etc….)
- Further analysis to classify data, study correlations and make predictions
  - algorithims
  - PCA-principal components analysis
  - CA-cluster analysis
  - SOM-self organizing maps
  - linear algebra, iterative learning
  - PCR- principal component regression
  - PLS-partial least squares regression
  - BPN-backpropagation neural networks
- Classification of samples and correlation of data with known results i.e. analytical and sensory measurements in database

Application areas for EN

- Quality and process monitoring of food
  - meat, fish, vegetables, fruits, oils, dairy products, coffee, alcoholic beverages etc.
- Packaging
  - tainting
- Flavor and fragrances
- Paper industry
- Biotechnology
- Car industry
  - emissions from exhaust system
  - emissions from passenger compartments
- Textile floor coverings
- Medical field
- Mine detection
  - dogs

Detection of fish freshness using EN

- Handheld EN -
  - device moved over an open product (on-line or spotcheck)
- EN adapted to various sizes of containers
  - 100g - 1000g containers
  - fish boxes, barrels or tubs 20-500 kg
- EN measurements of samples performed in the laboratory

Catching day labelled

Electronic Nose instruments used in research at Rf

- FreshSense, Iceland
  - static sampling system
  - electrochemical gas sensors CO, H_2S, NO, NO_2, SO_2 NH_3
- Bloodhound, UK
  - dynamic sampling system
  - DLC sensors
  - Polyconducting polymer sensors

Odor profile of fish and volatile compounds

FRESHNESS

- FRESH → C6-C9 carbonyls and alcohols (ppb)
- FLAT → short chain (C2-C6) alcohols, carbonyls and esters (ppm)
- SWEET
- STALE → volatile amines (NH_3, TMA) (ppm)
- PUTRID → volatile sulfur compounds (H_2S, CH_3SH) (ppm)

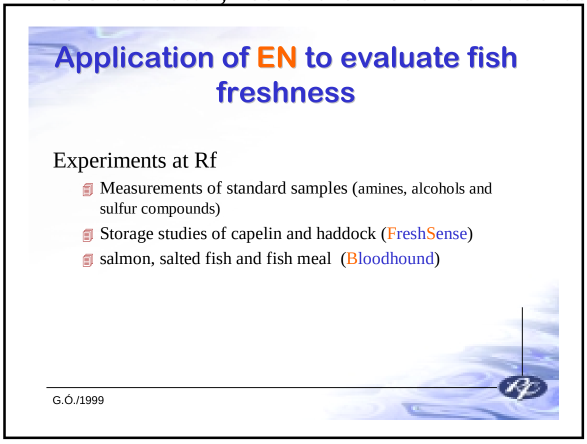
SPOILAGE

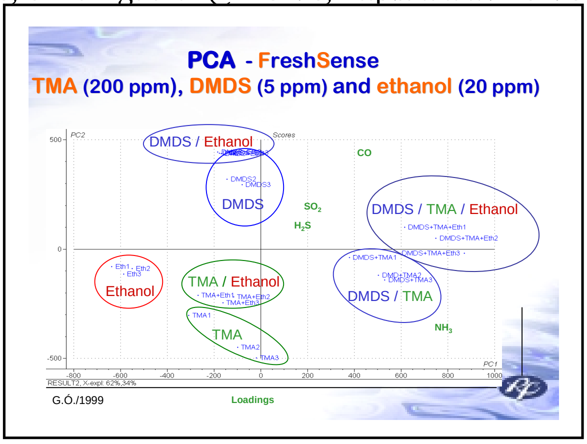
Sensory Evaluation and Quality, Workshop VIII,

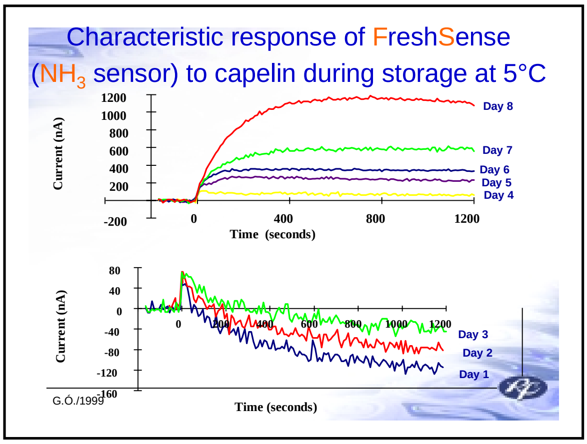
Reykjavík, Iceland, September 9-11, 1999

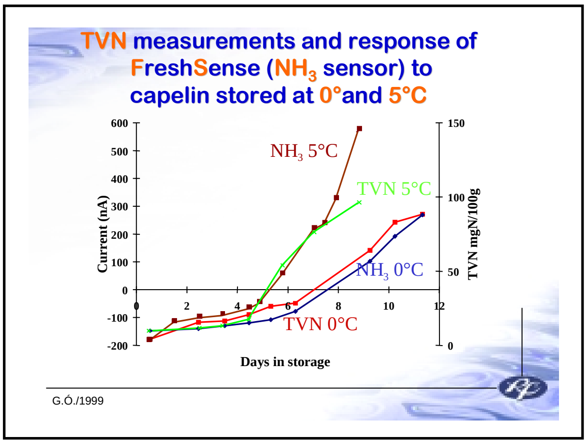
Electronic Nose Instead of Sensory Analysis?

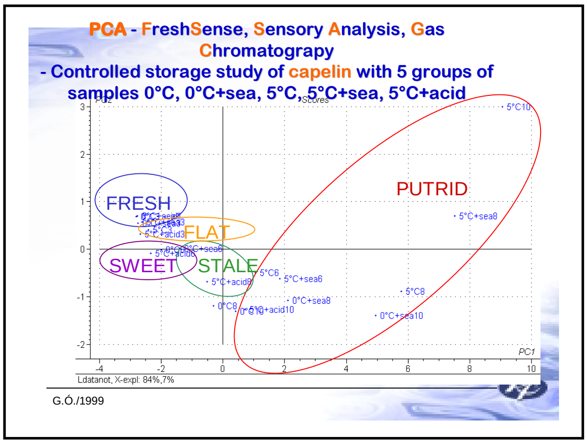
G. Olafsdóttir, Icelandic Fisheries Laboratories, e-mail gudrun@rfisk.is, http://www.rfisk.is

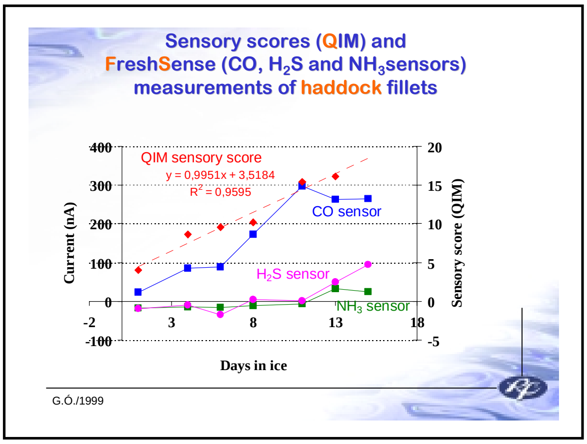












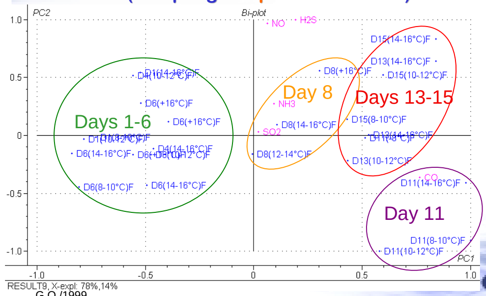
Sensory Evaluation and Quality, Workshop VIII,

Reykjavík, Iceland, September 9-11, 1999

Electronic Nose Instead of Sensory Analysis?

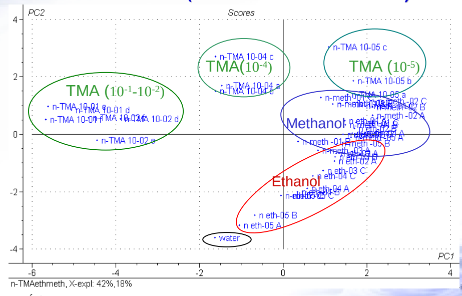
G. Olafsdóttir, Icelandic Fisheries Laboratories, e-mail gudrun@rfisk.is, http://www.rfisk.is

PCA of FreshSense measurements of haddock during storage in ice (fillets) (sampling temperature varied)



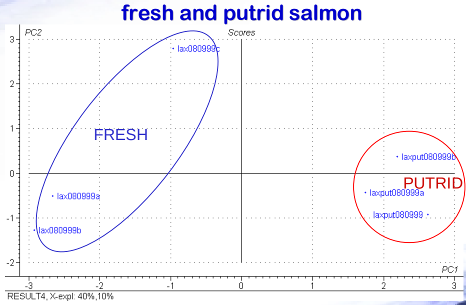
G.O./1999

PCA - Bloodhound DLC sensor responses to TMA ethanol and methanol (conc. 10^{-1}-10^{-5} in water)



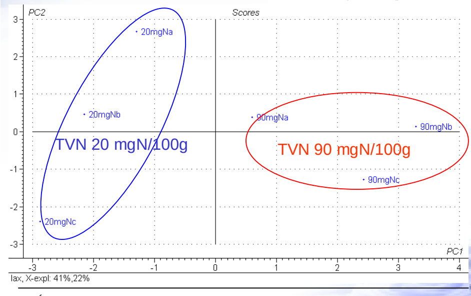
G.Ó./1999

PCA - Bloodhound BH213 fresh and putrid salmon



G.Ó./1999

PCA - Bloodhound BH213 salted fish of different quality



G.Ó./1999

Electronic Nose research at Rf
Conclusions

EN can discriminate between:

- standard samples and mixtures of very volatile compounds
- different spoilage level or quality of fish products
  - capelin and haddock - FreshSense
  - salmon and salted fish - Bloodhound
- Previous experiments at Rf using the EN FreshSense for:
  - quality evaluation of herring, cod, shrimp, cod roe, fishmeal
  - spoilage potential *Pseudomonas* and *Shewanella* in fish extract
  - odour evaluation in fish meal factories

G.Ó./1999

Future prospects for EN

- EN can complement techniques in analytical chemistry and sensory evaluation
- EN can be advantageous for toxic and bad smelling odours that can not be evaluated by human panelists
- Cheap and small on-line EN instruments for fast analysis of volatile compounds are needed in quality and process control

G.Ó./1999

Electronic Nose Instead of Sensory Analysis?

G. Olafsdóttir, Icelandic Fisheries Laboratories, e-mail gudrun@rfisk.is, http://www.rfisk.is

Future prospects for EN in the fish industry

- Important to verify freshness of fish products and ensure traceability in the fish sector (i.e.fish auctions, fish producers and distributors)
  - EN can detect fish freshness and spoilage
  - rapid mesurements of freshness or quality are needed to use in models to predict shelf-life of products
  - valid, rapid methods i.e EN are needed to monitor quality labels
- Implementation of EN in the fish industry
  - validation and standardisation of EN techniques is needed

G.Ó./1999

Acknowledgements

Icelandic Research Council for funding research on the development of the EN FreshSense

EU for financial assistance in following projects:

- “Electronic Profiling of Food and Bevarage Odour for Quality Determinations”
  - FAIR CT98 3436
- “Fish quality labelling and monitoring”
  - FAIR CT98-4174 http://www.rivo.dlo.nl/mktv/

Staff at Rf:

- Emilía Martinsdóttir, Áslaug Högnadóttir, Sigrún Jónsdóttir and Luca Laghi

G.Ó./1999