

DEVELOPMENT OF A SURFACE ACOUSTIC WAVE GAS SENSOR FOR ORGANOPHOSPHORUS NERVE AGENTS EMPLOYING LANTHANIDE COMPOUNDS AS THE CHEMICAL INTERFACE

M. S. NIEUWENHUIZEN* and J. L. N. HARTEVELD

TNO Prins Maurits Laboratory, P O Box 45, 2280 AA Rijswijk, The Netherlands

(Received 9 April 1993 Revised 18 June 1993 Accepted 14 July 1993)

Summary—The results of a study dealing with surface acoustic wave gas sensors for organophosphorus compounds such as nerve agents are described. Several lanthanum coordination compounds were applied as the chemical interface. The various sensors prepared were challenged with both the nerve agent sarin and the simulant dimethyl methylphosphonate. Many aspects were studied, such as sensitivity, selectivity, reversibility and response rate as well as the effect of temperature and structural features.

Detection limits down to 0.1 ppm were found. Response rates require further improvement. Degradation phenomena were observed which in some cases yielded irreversible responses. The selectivity for organophosphorus compounds was found to be promising.

There is a lack of modern gas sensors capable of real-time monitoring of organophosphorus compounds such as nerve agents or certain pesticides. In the future, this lack will become a serious deficiency as the present family of detection equipment is rather slow and needs a lot of manpower for sampling, analysis and servicing. Furthermore, the existing detectors are not readily adaptable to new chemical agents.

General requirements for this type of gas sensor will be: high sensitivity (ppb range), short response times (seconds), reversibility because of the monitoring function and high selectivity resulting in low false alarm rates. In addition, small size, light weight, ruggedness, long shelf life and operational life and low cost are important.

A number of examples have been reported in the literature on this subject; for instance, potentiometric sensors, optical sensors and piezoelectric crystal sensors employing bulk acoustic waves (BAWs). In all cases, most of the work concerned the finding of suitable coatings in order to detect organophosphorus pesticides as such or as model compounds for nerve agents.

This paper reports a study concerning gas sensors for organophosphorus compounds em-

ploying surface acoustic wave (SAW) devices following our work on SAW gas sensors for NO_2 .^{1,2}

In 1970 Slobodnik³ discovered the gas loading effect on surface acoustic waves. Wohltjen and Dessy⁴ described the application of such devices as chemical sensors, detectors in gas chromatography or for materials research. Two recent review papers^{5,6} gave an introduction of the basic principles and an overview on what happened in the field of development of SAW as well as the closely related BAW chemical sensors.

A SAW is generated by an interdigital transducer which is a combination of a piezoelectric medium and two interlocked comb-shaped electrodes. At some distance (8–10 mm) a second interdigital transducer converts the acoustic signal back into an electrical signal. In this way a so-called delay-line is created. Changes of the physical characteristics of such a delay-line, its mass, temperature, pressure or electrical conductivity, cause changes in the propagation velocity of the wave, which can be measured very sensitively as frequency changes when the sensor forms a component in an oscillator circuit. When the change in physical characteristics is caused by the presence of a chemical compound in the surrounding atmosphere, a SAW gas sensor is obtained. To satisfy the required detection characteristics a selective interaction

*Author for correspondence

of the gas with the SAW delay-line is needed. Therefore a coating or chemical interface is applied, consisting of a material which selectively interacts with the analyte.

Acoustic sensors appear to be very interesting because of their low detection limits and their relative simplicity. To obtain enhanced sensitivities higher sensor frequencies may be used. To allow the use of higher frequencies piezoelectric crystals should become very thin and therefore become very weak whereas in the case of SAW sensors this can be afforded through adaptation of the interdigital transducer and additional adaptations in the electronic system. Because a SAW sensor uses only the surface, the production of very small silicon chips, containing both the sensor and the electronic system, becomes possible. In the area of chemical interface design two basic concepts can be mentioned: a chemical approach and a biochemical approach. In the first category tailor-made organic compounds will act as the chemical interface yielding chemical sensors, whereas in the second category biochemical interfaces which are already created by nature, such as antibodies, enzymes or receptors will be utilized, thereby yielding biochemical sensors.

In the literature a number of examples is found dealing with acoustic (BAW and SAW) sensors for organophosphorus compounds. Recently a review was published dealing with this type of sensor.⁷

BAW sensors

Guilbault *et al.*⁸⁻¹⁴ studied various salts of heavy metals and some organic compounds for the detection of the nerve agent simulant diisopropyl methylphosphonate (DIMP). Balog *et al.*¹⁵ tested eight different chemical interface materials with the nerve agent sarin (GB). No responses were observed, but some materials responded to DIMP. Oxime systems have been reported by Olofsson *et al.*^{16,17}

Because the enzyme acetylcholinesterase is being inhibited by organophosphorus compounds this biochemical interface has been studied (in the gas phase) by van Sant¹⁸ and Guilbault *et al.*^{19,20} Furthermore, Guilbault *et al.*^{21,22} reported on the use of antibodies for the detection of parathion.

SAW sensors

A large number of studies of US Defence related groups²³⁻³⁵ used DIMP, dimethyl

methylphosphonate (DMMP) or tributyl phosphate (TBP) as model compounds and to some extent nerve agents themselves to test both small organic molecules or polymers as chemical interfaces. Most of the chemical interfaces were compounds with a limited amount of selectivity. However, as these research groups adhere to the concept of sensor arrays together with the use of pattern recognition techniques, they did not look for the ultimate selectivity of a single array element.

Recently Kepley *et al.*³⁶ described the use of simple copper coordination compounds for the detection of organophosphorus compounds but very little was revealed about their sensitivity.

In our laboratory the use of coordination compounds was postulated for the selective detection of organophosphorus compounds. A number of papers indicate a rather strong interaction between certain metal ions and organophosphorus compounds. Van de Berg *et al.*³⁷ and Ward *et al.*³⁸ used lanthanide compounds as so-called NMR shift reagents. Also, Guilbault *et al.*^{39,40} found rather strong interactions between DIMP and a number of lanthanide chlorides, reflected in a change of the infrared stretching frequencies of the P=O bond. Hellmuth and Mirzai⁴¹ found a large influence of TBP on the gas chromatographic properties of hexafluoroacetylacetonates of lanthanides and actinides. The interaction and therefore potential selectivity can be influenced by the type of co-ligands attached to the metal ion both in a steric and an electronic way. This paper describes the testing of SAW sensors applied with coordination compounds of the lanthanum(III) ion and aminopolycarboxylic acid residues with different functional moieties. It is to be expected that the tricarboxymethylamino moiety binds a lanthanide ion which itself binds the organophosphorus compounds through interaction with the oxygen atoms surrounding the phosphorus atom. A fourth carboxylic group in the co-ligand may be used to chemically immobilize the material to a sensor surface.

The various SAW sensors prepared have been challenged with both the nerve agent sarin [GB = ((CH₃)₂CHO)(CH₃)POF] and the simulant DMMP [= (CH₃O)₂PO(CH₃)]. Many aspects such as sensitivity, response and recovery rates, reversibility and selectivity as well as the effect of temperature and structural effects have been studied.

EXPERIMENTAL

Materials

The SAW sensors used in this study were STX-quartz dual delay-line devices (one measuring delay-line and an uncovered reference delay-line) with a centre frequency of 78 MHz provided with aluminium interdigital transducers. The sensors were obtained from Xensor Integration BV, Delft, The Netherlands.

The following chemical interface materials have been synthesized at TNO PML. The chemical nature as well as the purity of the resulting products have been established by ^1H NMR. The ^1H NMR spectra were recorded with a Varian XL-100 spectrometer with TMS as an indirect internal standard.

La(III) N,N,O-tricarboxymethyl tyrosine (LaTCMT). To a mixture of 2.72 g of tyrosine (15 mmol) in 20 ml of water 2.25 ml of 6.75M aqueous NaOH was added in order to dissolve the tyrosine. Subsequently, 10.5 g of sodium chloro acetate (90 mmol) in 20 ml water was added. While heating the mixture to 70°C the pH decreased from 10 to 9 due to the formation of HCl. Over a period of 6 hr 10 ml of the NaOH solution was added slowly in order to maintain the pH at 10, which after this period was raised to 11. After cooling, the reaction mixture was stirred for 24 hr at room temperature. After acidification to pH = 5.5 with concentrated HCl 5.6 g of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ in 25 ml of water was added in order to precipitate the lanthanum salt. White crystals were filtered off and washed three times with a water/ethanol mixture (1:1). After drying in vacuum at 60°C the yield was 6 g of LaTCMT. ^1H NMR (D_2O) δ 3.36 (m, CH_2 , 2H), 4.31 (d, CH_2 , 4H), 4.69 (m, CH, 1H), 4.76 (s, CH_2 , 2H), 7.00 (d, arom H, 2H), 7.29 (d, arom H, 2H).

La(III) N,N-dicarboxymethyl glutamic acid (LaDCMG). Glutamic acid was treated with sodium chloro acetate and $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ in the same way as described above for tyrosine to obtain LaDCMG. ^1H NMR (D_2O) δ 2.26 (m, CH_2 , 2H), 2.75 (m, CH_2 , 2H), 4.09 (m, CH, 1H), 4.35 (s, CH_2 , 4H).

2-amino hexadecanoic acid (BHA). Ten grams of 2-bromo hexadecanoic acid (30 mmol) and 300 ml of a 25% aqueous ammonia were heated at 50°C. During the first 2 hr of the reaction vigorous foaming occurred. After 2 hr 5 g of ammonium carbonate was added and the mixture was stirred during 20 hr at 50°C. After cooling the mixture was filtered. The residue

was washed successively two times with 100 ml of 1M hydrochloric acid, with water until the pH value reached 6, with 50 ml of methanol and 50 ml of diethyl ether. The product was dried at 50°C and yielded 7.3 g of 2-amino hexadecanoic acid. ^1H NMR (CF_3COOD) δ 0.91 (t, CH_3 , 3H), 1.36 (m, CH_2 's, 26), 2.16 (m, βCH_2 , 2H), 4.41 (t, CH, 1H).

La(III) 2-bis(carboxymethyl)amino hexadecanoic acid (LaBHA). The 2-amino hexadecanoic acid was converted to BHA by carboxymethylation as described above for tyrosine. BHA was treated with $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ in the same way as described above for tyrosine to obtain LaBHA. ^1H NMR (CF_3COOD) δ 0.89 (m, CH_3 , 3H), 1.36 (m, CH_2 's, 26), 2.20 (m, βCH_2 , 2H), 4.63 (m, OCH_2 , 2H), 4.63 (m, CH, 1H).

Methods

Vapour generation and SAW sensor testing system. Mixtures of the vapour of DMMP (obtained from Janssen Chimica) or GB (synthesized at TNO PML) and air were generated from a liquid source at 30°C in the SAW sensor testing system developed at TNO PML.⁴²

In order to prevent decomposition of GB inside the evaporation vessel dry nitrogen (<1% relative humidity) was used as the primary diluting gas stream. For further dilution and as a reference gas stream pressurized air (5–10% relative humidity) was used. The presence of dry nitrogen in the final mixture caused slight differences between the sample gas stream and the reference gas stream with respect to oxygen content and relative humidity. This difference did not cause a sensor response as has been proved by testing blank gas streams. To prevent any effect of ageing of the liquid source, for every new sensor tested with GB a fresh source was introduced in the evaporation vessel. An automated, reliable and safe system for testing SAW gas sensors has been developed.⁴² The system includes the possibility to generate and/or dilute almost any gas or vapour and can easily be adapted for testing sensors or equipment other than SAW sensors. A highly efficient way of testing has been realized for unattended operation in a safe way. A large range of concentrations is achievable by the option of single-stage or two-stage dilution. The reliability of the gas generation system is guaranteed by the continuous monitoring of the concentration of the vapour or gas generated by using mass flow controllers. Both monitors and mass flow controllers are periodically calibrated.

For the monitoring of the phosphorous containing vapours a Meloy Instruments flame photometer has been used while all other compounds were monitored with a Foxboro Miran infrared vapour monitor at the appropriate wavelength.

Application of chemical interfaces

The dried drop method was used to apply the chemical interface material to the sensor surface. Therefore the following solutions or suspensions in an ethanol/water mixture (1:1) were prepared of LaTCMT, LaDCMG, LaBHA, $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and BHA and treated ultrasonically (Ultrasonic bath Bransonic 1200) to yield a 0.1% mixture. At a sensor temperature of 30°C, 5 μl of a solution was applied at the measuring delay-line of the sensor and the resulting frequency shift was noted. This procedure was repeated until the requested total frequency shift was attained. In Fig. 1 scanning electron micrographs of the coatings LaTCMT, LaDCMG and LaBHA are depicted. It is noted that the spreading of the dried drops of the coatings varies from one coating to the other, *i.e.* in the case of LaTCMT and LaBHA a rim of dried material is observed whereas in the case of LaDCMG almost homogeneous spreading is observed. With respect to the sensitivity of the chemical interface the coverage of the quartz is important. In the case of LaTCMT all material is present in the rim and hardly any material sits next to the rim. In the case of LaDCMG there is no rim, but a lot of bare quartz is observed in between the particles. In the case of LaBHA the best morphology is observed in terms of sensitivity, because apart from the rim the whole surface area is covered with the chemical interface material.

In Table 1 the characteristics (determined at 30°C) of the sensors used in this study such as the frequency, the amount of chemical interface as well as the resulting frequency shift, the medium-term drift and the peak-to-peak noise are given.

Scanning Electron Microscopy (SEM)

The surface structure and the elemental composition of the chemical interfaces were determined with a Philips SEM 515 Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-ray analysis (EDX) facility. Investigation with SEM of the poorly conductive lanthanum salts requires the application of a conductive coating to avoid charging. A

thin carbon coating of a few nanometres was applied by thermal evaporation. SEM and EDX investigations were carried out at a primary electron energy of 10–15 keV.

X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) was performed using a Perkin-Elmer PHI 5400 ESCA equipped with a dual anode X-ray source and a concentric hemispherical analyser. $\text{Mg-K}\alpha$ radiation (1253.6 eV) was employed at 400 W.

RESULTS AND DISCUSSION

Carboxymethyl derivatives of tyrosine and glutamic acid have been synthesized resulting in La(III) *N,N,O*-tricarboxymethyl tyrosine (LaTCMT) and La(III) *N,N*-dicarboxymethyl glutamic acid (LaDCMG) (Fig. 2). Also, La(III) 2-bis(carboxymethyl)amino hexadecanoic acid (LaBHA) containing a long hydrophobic chain (C_{14}) has been synthesized. In a later phase of the project, the latter compound is meant to be attached to the sensor in a physical way by Langmuir-Blodgett film deposition.

In the case of the experiments described in this paper all chemical interfaces have been applied by the dried drop method: a drop of a solution was placed in the delay-line area and dried at 30°C. This procedure was repeated until the requested frequency shift was attained. This frequency shift is supposed to be a measure of the amount of chemical interface material present at the sensor surface and has been used by us and many others in the SAW sensor literature as a pseudo layer thickness, assuming a simple relationship between frequency change and mass, which is the thickness at a fixed surface area and density. During the experiments it turned out that, at least in our case, the assumption is not valid. The method was calibrated by relating the frequency shift to the amount of mass of chemical interface materials which was actually applied, known from the volume of the drops and the concentration. The calibration curves for the three compounds LaDCMG, LaTCMT and LaBHA are shown in Fig. 3.

In this figure it is clearly shown that the frequency shift is not only a function of the amount of mass applied. In that case the three curves would coincide. It is noted that LaBHA differs from the other two compounds. This may be caused by differences in morphology, *i.e.* the way of spreading of the drop during drying

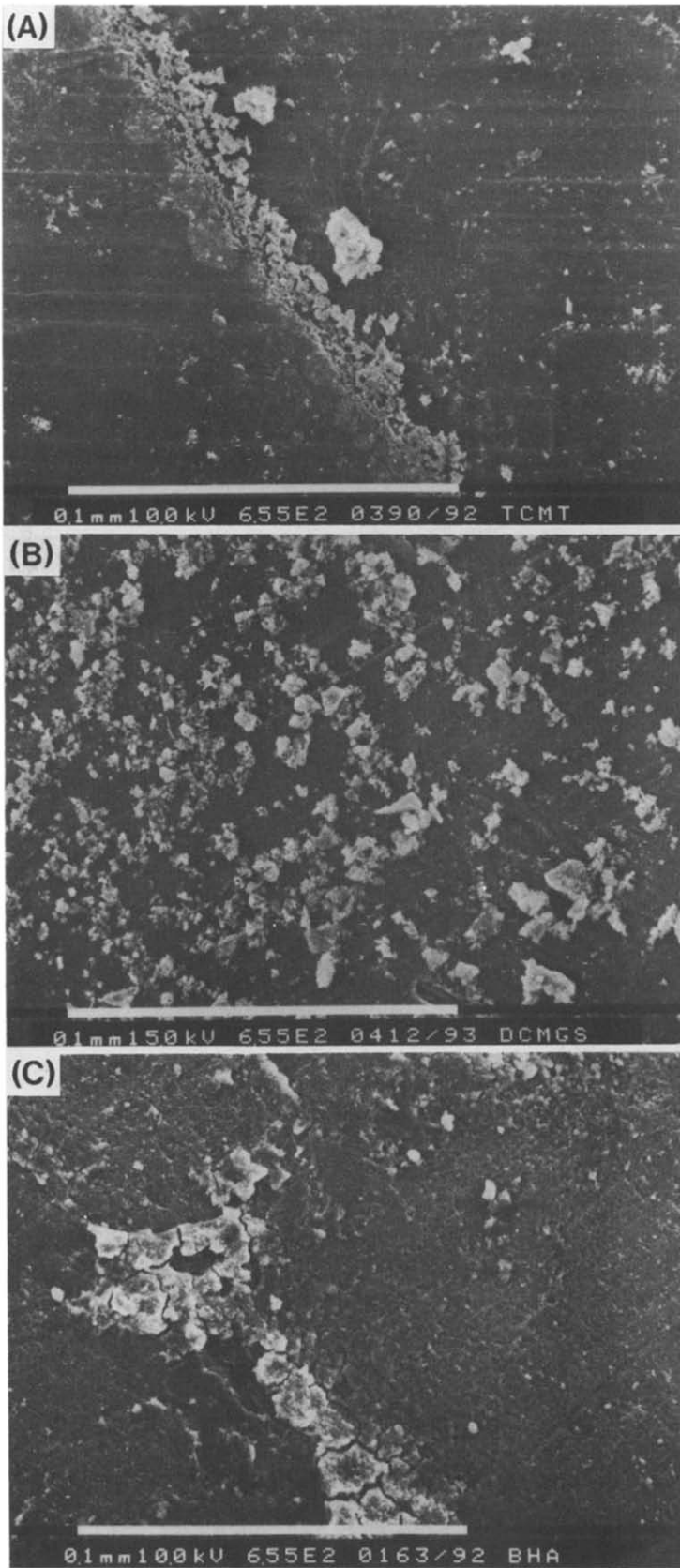


Fig 1 Scanning electron micrographs (650 \times) of (from top to bottom) the chemical interfaces LaTCMT, LaDCMG and LaBHA

Table 1 Values of the base frequency (F_0), the mass of the chemical interface material both expressed as frequency shift (ΔF) and the mass change (ΔM), drift (D) and peak-to-peak noise (N) at 30°C of the sensors tested

Sensor code	CI*	F_0 (MHz)	ΔF (kHz)	ΔM (μg)	D (Hz/min)	N (Hz)
GLU194	LaDCMG	78.51	11	8.6	-0.06	11
TYR188	LaTCMT	78.88	30	12.2	-0.09	10
HDZ192	LaBHA	78.85	50	5.4	0.14	15
HDZ193	LaBHA	78.85	51	5.4	0.27	11
HDZ161	LaBHA	78.48	57	—†	0.36	5
HDZ162	LaBHA	78.48	60	—†	0.20	15
HDZ163	LaBHA	78.47	69	—†	-0.15	30
LAC164	LaCl ₃	78.50	50	—†	-0.23	15
HDZ158	BHA	78.85	45	—†	0.28	35

*CI = chemical interface identity

†Frequency change has not been calibrated against mass change

as can be observed in Fig. 1, elasticity or conductivity (the long non-polar CH₂-string of LaBHA) which are all properties that are known to affect the SAW sensor frequency.

When SAW sensors with different amounts of chemical interface material are to be compared they are better compared on a real mass basis than indirectly on the basis of a frequency shift.

Above a certain mass loading the decrease of the SAW signal amplitude cannot be compensated for by the electronics and oscillation stops. It turned out that the maximum mass load of this 78 MHz SAW sensor is about 10 μg .

The results of the measurements are presented as dual delay-line measurements to correct for aspecific effects of temperature and pressure. The data were corrected for the frequency changes resulting from the adsorption of DMMP, GB or other compounds at the uncovered quartz surface of the reference delay-line. In Fig. 4 the response curves of both DMMP and GB of the reference delay-line of a 78 MHz quartz SAW device at 30°C are shown. The

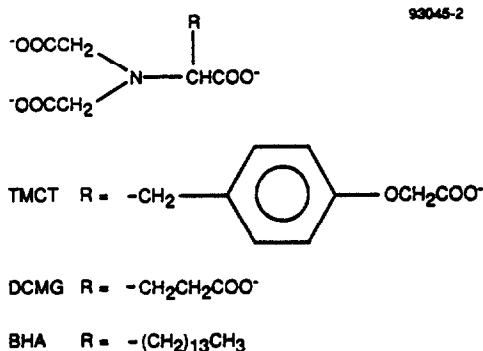


Fig 2 The three lanthanide complexes derivatives of nitrilotriacetic acid studied in this report

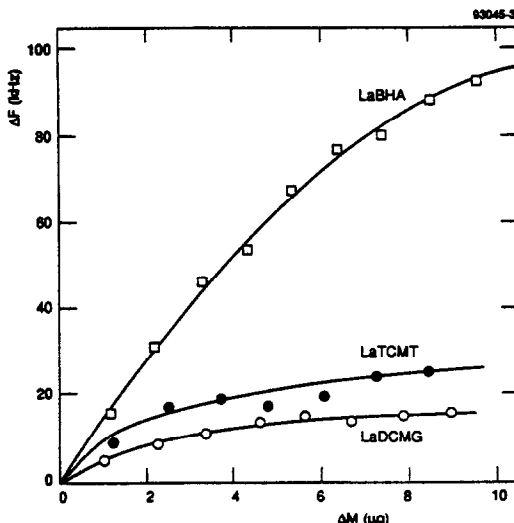


Fig 3 Relation between the frequency shift (ΔF) of a 78 MHz SAW sensor and the mass (ΔM) of chemical interface material applied LaTCMT (●), LaDCMG (○), LaBHA (□)

response of the reference delay-line was always accounted for but was usually negligible

Measurements with DMMP

In Fig. 5 a number of response curves for DMMP of the different chemical interface materials at 30°C are presented expressed as the frequency shift normalized to the amount of mass of the chemical interface material present *vs.* the concentration of DMMP. In Table 2 the normalized sensitivity (response divided by the concentration) to 5 ppm DMMP are listed together with the 80% response and recovery times.

From the results presented in Fig. 5 and Table 2 it can be observed that LaBHA shows the largest sensitivity for DMMP. It should be

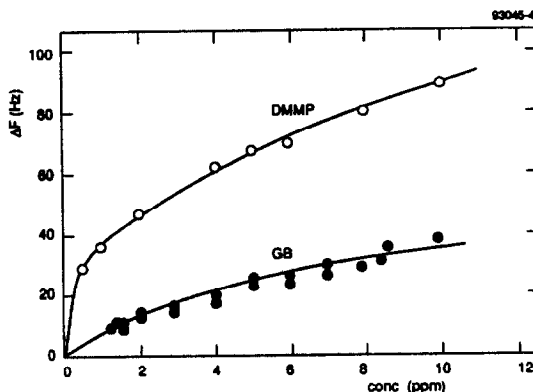


Fig 4 Response of the reference delay-line of a 78 MHz SAW device expressed as the frequency shift (ΔF) due to adsorption of DMMP (○) or GB (●) at 30°C.

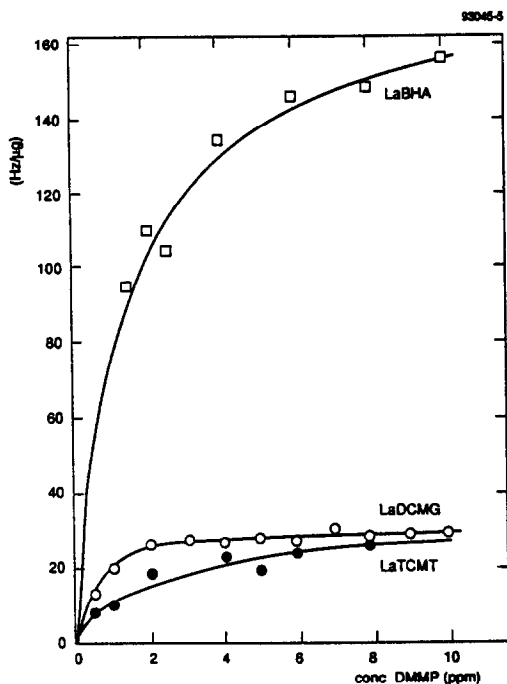


Fig 5 Normalized response (in Hz/ μg) to DMMP of LaTCMT (●), LaDCMG (○) and LaBHA (□) at 30°C

noted that there might be a similarity between the high sensitivity for DMMP of the LaBHA coated sensor and the high mass response of the sensor due to the application of the chemical interface at the sensor. The morphology (see Fig. 1) may also be an important factor. From the shape of the curves in Fig. 5 it is shown that the adsorption at the chemical interface is almost saturated, especially in the case of LaTCMT and LaDCMG. Therefore one might expect higher sensitivities, and therefore low detection limits, in the steeper part of the curves provided the signal-to-noise ratio would allow accurate measurements. In the case of sensor HDZ192 containing LaBHA a detection limit of 0.1 ppm (0.5 mg/m³) at a signal-to-noise ratio of 5 is estimated.

Differences in sensitivity of the various chemical interfaces result both from different affinities but may also result from differences in morphology. The scanning electron micrographs

Table 2 The sensitivity normalized to the layer mass at 5 ppm DMMP as well as the 80% response times (RT_{80}) and recovery times (RCT_{80}) of LaTCMT, LaDCMG and LaBHA at 30°C

Sensor code	Chemical interface	Sensitivity (Hz/ppm μg)	RT_{80} (min)	RCT_{80} (min)
TYR188	LaTCMT	4.5	2	18
GLU194	LaDCMG	5.3	2	27
HDZ192	LaBHA	28.0	4	13

presented in Fig. 1 show that in the case of LaBHA, the most sensitive coating, the material is well spread on the ground surface of the former droplet. In the case of the other chemical interfaces the major part of the material was found at the outer rim of the former droplet. In order to study the effect of temperature on the sensitivity for DMMP, sensor HDZ162 was tested at 30 and 50°C and sensor HDZ163 was tested at 70°C. Both sensors contained the chemical interface LaBHA. As in this case the frequency shift due to the presence of the chemical interface was not calibrated against the applied mass, the sensitivity was normalized to that frequency shift rather than to the applied mass. Table 3 shows the results of these measurements. As expected, the sensitivity for DMMP decreased at increasing temperature whereas, especially, the recovery became faster.

From DMMP measurements with the ligand BHA and LaCl₃ (without the ligand) information can be obtained about the role both the ligand and the central lanthanum ion play. In Table 4 the results of these measurements at 30°C are listed.

From Table 4 it can be seen that the lanthanum ion in the form of its chloride salt shows affinity towards DMMP. This affinity is improved by a factor of 5 upon the addition of a tricarboxylic ligand, which apparently brings the lanthanum ion into an accessible configuration to coordinate with the phosphorylic group of organophosphorus compounds. DMMP measurements with BHA showed no difference between the occupied and the reference delay-line of the sensor, *i.e.* the sensitivity was zero expressing the important role of the central ion.

Measurements with GB

After the measurements with DMMP the sensors were tested with GB at 30°C. From previous experiments⁴³ it was known that the presence of products resulting from the hydrolysis of GB during the vapour generation (*e.g.*

Table 3 The sensitivity at 5 ppm DMMP normalized to the frequency change resulting from the mass of the chemical interface as well as the 80% response times (RT_{80}) and recovery times (RCT_{80}) of LaBHA at 30, 50 and 70°C

Sensor code	Temperature	Sensitivity (Hz/ppm kHz)	RT_{80} (min)	RCT_{80} (min)
HDZ162	30	8.2	10	75
HDZ162	50	3.2	10	30
HDZ163	70	1.4	8	11

Table 4 The sensitivity at 5 ppm DMMP normalized to the frequency change resulting from the mass of the chemical interface at 30°C for the chemical interfaces LaHBA, BHA and LaCl₃

Sensor code	Chemical interface material	Sensitivity (Hz/ppm kHz)
HDZ161	LaBHA	1.1
LAC164	LaCl ₃	0.2
HDZ161	BHA	0

hydroxy GB or hydrogen fluoride) are responsible for a peculiar response behaviour: a reversible and relatively fast response accompanied by an irreversible and slow response. Therefore, during the present experiments, for every other sensor a fresh liquid source of GB was used, together with using dry nitrogen as the primary diluting gas stream in order to prevent hydrolysis of GB at the liquid/gas interface of the GB source. When GB is being hydrolysed near the source, the reference delay-line would also show a peculiar response behaviour, but during these experiments this was not the case. This fact, as well as chemical analysis of the composition of the vapour stream, proved that no products resulting from the hydrolysis of GB were present in the generated GB vapour stream.

During the tests with GB, surprisingly, especially in the case of LaBHA and LaTCMT, the same peculiar irreversible response behaviour as described above was observed, as can be seen in Fig. 6 showing typical responses of the sensors to about 9 ppm of GB. In the case of LaDCMG only the first few responses were partly irreversible.

From plots such as the ones presented in Fig. 6 a reversible part of the response could be derived. A plot showing this response *vs.* the concentration of GB is depicted in Fig. 7. It should be noted that all measurements presented in Fig. 7 are performed in the order from low to high concentrations of GB. The sensitivity at 5 ppm of GB as well as the response time and recovery time are presented in Table 5.

From Tables 5 and 2 it can be observed that the sensitivity for GB is smaller than that for DMMP with LaTCMT and LaBHA, although LaBHA still shows the highest sensitivity. In the case of sensor HDZ194 containing LaBHA a detection limit of about 0.1 ppm (0.5 mg/m³) at a signal-to-noise ratio of 5 is estimated. The response times for GB are higher than the ones for DMMP, while the recovery times are lower than the one for DMMP. In general, the response rates are far from practical with respect

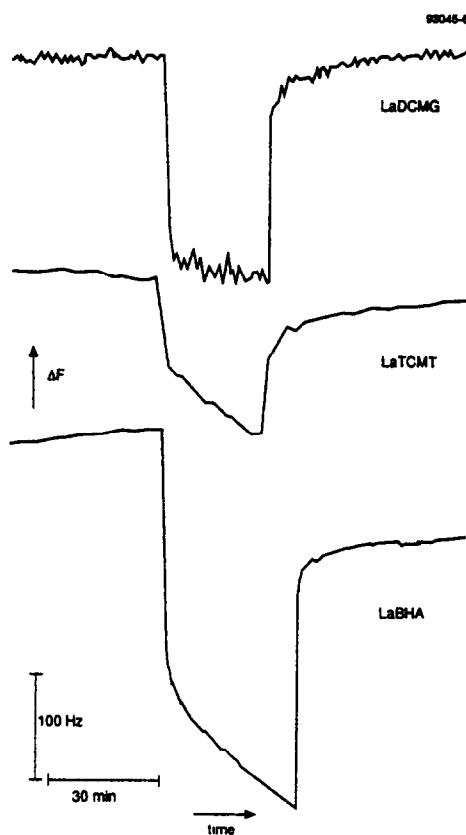


Fig. 6 Response plots of the various sensors applied with LaTCMT (a), LaDCMG (b) and LaBHA (c) when exposed to about 9 ppm of GB at 30°C

to monitoring or even warning applications. Alternative ways of applying the chemical interface may result in a better spreading as well as a different morphology which may yield both higher sensitivities and faster responses.

In order to study temperature effects, in Table 5 the measurements at 50°C and 70°C are also presented. The results indicate a similar temperature effect on the reversible part of the

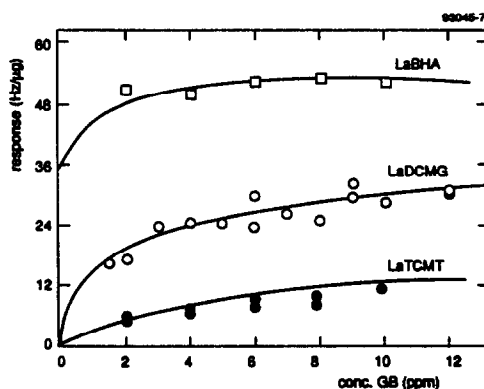


Fig. 7 Normalized response (in Hz/μg) to GB of LaTCMT (●), LaDCMG (○) and LaBHA (□) at 30°C

Table 5 The sensitivity normalized to the layer mass at 5 ppm GB as well as the 80% response times (RT_{80}) and recovery times (RCT_{80}) of LaTCMT, LaDCMG at 30°C and LaBHA at 30, 50 and 70°C

Sensor code	Chemical interface	Temp (°C)	Sensitivity (Hz/ppm μ g)	RT_{80} (min)	RCT_{80} (min)
TYR188	LaTCMT	30	1.5*	5	15
GLU194	LaDCMG	30	4.8	6	15
HDZ192	LaBHA	30	10.0*	11	13
HDZ162	LaBHA	50	6*†	—‡	—‡
HDZ163	LaBHA	70	3*†	—‡	—‡

*Derived from the reversible part of the response

†Less accurate data due to small difference in reversible and irreversible response rates

‡No reliable results (see above)

response as in the case of DMMP (Table 3). Due to the fact that also the rate of the irreversible part of the response was increased, discrimination between the two response types was difficult. As a result the results at elevated temperatures are less accurate and reliable response and recovery rate data could not be derived either.

When looking at the irreversible part of the response to GB, it was found that its rate, expressed as the frequency change per unit time, is related to the concentration of GB as can be observed in Fig. 8.

The presence of hydroxy GB or other hydrolysis products in the vapour phase is completely excluded. Therefore the irreversible part of the response has to be the result of phenomena taking place at the sensor itself, *i.e.* the

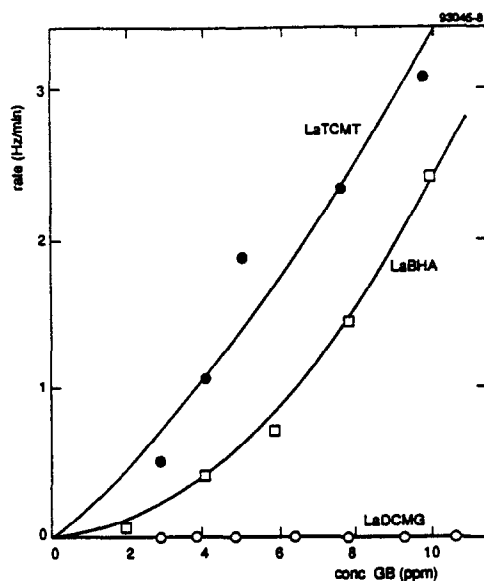


Fig 8 The frequency change per unit time of the irreversible part of the response of LaTCMT (●), LaDCMG (○), LaBHA (□) to GB at 30°C

adsorptive sites may be blocked by reaction products, *e.g.* resulting from hydrolysis or the formation of dimers. The high local concentrations of both GB and water (present in the diluting airstream of 5–10% relative humidity) at the chemical interface may enhance these reactions. Moreover, the strong interaction between the chemical interface and GB, which was supposed to yield a selective and sensitive sensor, may cause a catalytic effect on the reactions taking place. This explanation would exclude the catalytic effects in the case of LaDCMG which showed only reversible responses. The chemical nature of LaDCMG differs hardly from that of the other chemical interfaces. Therefore one would not expect large differences in the catalytic effects mentioned. In order to find a better explanation further studies (a check of the response to DMMP and surface analysis of chemical interface materials treated with GB) were initiated.

Further measurements with DMMP

In order to obtain an impression about the damage the reaction products of GB have caused to the chemical interfaces (irreversible adsorption at adsorptive sites), the sensors have again been tested with DMMP after exposure to GB in order to characterize them. Table 6 is showing the sensitivity before and after the measurements with GB. It is clearly observed that both sensors showing the irreversible responses (LaTCMT and LaHBA) to GB have become considerably less sensitive to DMMP, whereas the sensitivity of LaDCMG has not changed at all.

Elemental analysis and surface analysis studies

In order to provide further proof for the above-mentioned hypothesis that GB or degradation products of GB are responsible for the irreversible response behaviour, we tried to find remainders of GB at the surface of the chemical interface material after endured treatment with GB. One remainder would be the element P,

Table 6 The sensitivity at 30°C to 5 ppm of DMMP normalized to the layer mass LaTCMT, LaDCMG and LaBHA before and after the measurements with GB

Sensor code	Chemical interface	Sensitivity before GB (Hz/ppm \cdot μ g)	Sensitivity after GB (Hz/ppm \cdot μ g)
TYR188	LaTCMT	4.5	1.9
GLU194	LaDCMG	5.3	5.3
HDZ192	LaBHA	28.0	16.5

present in strongly adsorbing degradation products of GB. The formation of HF may be the result of the first step of the degradation of GB. HF is a highly reactive gas and may be adsorbed or chemisorbed by the chemical interface material right after its formation. Therefore the presence of the element F would also yield interesting information.

First of all, energy dispersive X-ray analysis, especially looking at the elements P and F, was performed with dried drops of about 0.1 mg of the chemical interfaces, both before and after treatment with GB (concentration of 100 mg/m³) of GB during 4 hr). Secondly, in order to obtain an additional indication of the presence of the elements P and F and concomitant structural and quantitative information, surface analysis was performed using XPS (X-ray Photoelectron Spectroscopy). The results of EDX and XPS analysis are presented in Table 7.

Due to the heterogeneity of the samples the results of XPS analyses can only be presented in a semi-quantitative way. The same applies to the EDX results because in some cases the amount of P or F was close to the detection limit. According to the XPS results in the case of untreated samples both LaTCMT and LaDCMG seem to contain F. This may be caused by the fact that due to the heterogeneity the elemental composition of the top layer of the underlying material (in this case aluminium) contributes to the result. Unfortunately no structural information could be derived from the XPS results.

From Table 7 it becomes very clear that the elements P and F appear in all samples, especially also in the case of LaDCMG, upon treatment with GB, whereas under the exper-

imental conditions applied GB itself will no longer be present at the chemical interface material. Even when F seemed to be present before treatment a clear increase of the amount of F was observed.

On the one hand, these results support the hypothesis of a damaged chemical interface material causing the observed irreversibility in the response to GB and the decreased responses to DMMP after treatment. On the other hand, the fact that the elements P and F are also present in LaDCMG, whose response to GB is hardly irreversible and whose response to DMMP has not been affected at all, demands an adapted explanation. Most probably GB is degraded by LaDCMG but its remainders hardly affect the response to GB or DMMP; *i.e.* the adsorptive site of LaDCMG is not affected by treatment with GB, whereas the adsorptive sites of LaTCMT and LaBHA are

Measurements with potential interfering compounds

In order to obtain an impression about the selectivity of the lanthanum complexes tested in this report, a fresh LaBHA sensor (HDZ193) was tested with a number of potential interfering compounds. These compounds represent different classes of organic and inorganic compounds. LaBHA was chosen, as it showed the largest sensitivity for organophosphorus compounds and was expected to interact the most strongly with non-polar organic compounds because of the large non-polar CH₂-chain.

In order to obtain reliable results the concentration of the interferences had to be raised significantly. They were usually measured in the

Table 7 Results of EDX and XPS analysis of thin layers of chemical interface materials before and after treatment with GB

Chemical interface	Before GB treatment				After GB treatment			
	EDX†		XPS		EDX†		XPS	
	%P	%F	P	F	%P†	%F†	P	F
LaTCMT	—‡	—‡	—‡		0.2 (±20%)	0.4 (±50%)		¶
LaDCMG	—‡	—‡	—‡		0.1 (±50%)	§	¶	¶
LaBHA	—‡	—‡	—‡	—‡	0.2 (±20%)	0.1 (±50%)		§

*Dried drops of about 0.1 mg of material were treated with GB (concentration of 100 mg/m³) for 4 hr

†In % w/w

‡Not present.

§Small relative amount present

||Medium relative amount present

¶High relative amount present

Table 8 The response and sensitivity of LaBHA (HDZ193) to different gases and vapours at 30°C

	Concentration (ppm)	Response (Hz)	Sensitivity (Hz/ppm μ g)
GB	5	285*	10.6*
DMMP	5	800	29.6
Ethanol	300	150	0.09
<i>n</i> -Hexane	300	-20	-0.01
Methyl ethylketone	300	50	-0.03
Ethylacetate	300	30	0.02
Toluene	150	30	0.04
Water	15,000†	1200	0.02
Ammonia	300	400	0.25
Nitrogen dioxide‡	300	5800	3.6

*Not tested with this sensor but calculated from HDZ192 (and derived from reversible part of response)

†In addition to the water present in the reference gas stream

‡Very slow, irreversible response

100–400 ppm concentration range (water up to 15,000 ppm) where the response curve (adsorption isotherm) did not show saturation phenomena yet. As a result of the higher concentrations the various responses cannot be compared in a proper thermodynamic way. Nevertheless, an impression of the selectivity of this type of chemical interface has been obtained. The results are presented in Table 8.

The responses of the sensor for the different interferences are compared with those for GB (not tested with this sensor, but calculated from another one) and DMMP.

From Table 8 it is observed that most compounds tested do not interfere more than 1% on a molar basis. It should be noted that in real situations some of these compounds, especially water, may be present in much larger quantities than the analyte itself. Only nitrogen dioxide, which was the last compound tested, interferes rather strongly and irreversibly, although its response is very slow when compared to all other compounds (hours *vs.* several minutes). It is probable that nitrogen dioxide is damaging LaBHA. When measuring the DMMP response afterwards it turned out to be only 30% of the initial DMMP response.

CONCLUSIONS

The following conclusions can be drawn with respect to the general aspects of the interpretation of SAW sensor results. In order to compare different chemical interfaces, the effect of different amounts of the chemical interface present at the delay-line of a SAW sensor is better accounted for by normalizing to the mass than to the concomitant frequency shift. It was

found that the application of the same mass of different chemical materials yield different frequency shifts indicating that not only mass is responsible for that frequency shift. As a result normalizing to frequency shifts does not automatically correlate with normalizing to mass. Different morphologies as well as elastic and electrical effects may be responsible for this behaviour.

The lanthanum complexes studied in this paper exhibit affinity towards organophosphorus compounds. The observed sensitivity is a result of coordinative interaction of the lanthanum ion, configured in a favourable position by the tricarboxymethylamino moiety, with the phosphorylic group of the organophosphorus compounds.

The best sensitivity to DMMP and the nerve agent GB was obtained with La(III) 2-bis(carboxymethyl)amino hexadecanoic acid applied as a dried drop on a 78 MHz SAW sensor. The detection limit of this sensor is estimated at 0.1 ppm (0.5 mg/m³) of DMMP or GB.

The sensitivity to DMMP decreases at elevated temperatures, whereas response and recovery become faster.

Both the ligand NHA without the lanthanum ion and the lanthanum ion without any ligand showed worse sensitivity to DMMP indicating both the importance of the central ion as well as the tricarboxymethylamino moiety of the ligand. The response to DMMP is reversible, but the response rate is low. Unfortunately, the responses of a number of chemical interfaces to GB show a partly irreversible component. This phenomenon is probably caused by the catalytic activity of the chemical interface, *i.e.* a strong interaction between the chemical interface and GB; on the one hand, the chemical interfaces were supposed to yield selective and sensitive sensors but, on the other hand, they are inducing chemical reactions. This phenomenon is very important from the point of view of philosophy of designing suitable chemical interfaces. Sometimes interactions may be chosen that are too strong, especially in the case of reactive analytes. Surface analysis of chemical interfaces treated with GB showed an increased amount of the elements P and F indicating the presence of degradation products of GB while the presence of GB itself is excluded. In one case the presence of degradation products did not affect the response to GB or to DMMP; La(III) *N,N*-dicarboxymethyl glutamic acid showed only reversible responses with a sensitivity for

GB of 5 Hz/ppm · μg and an 80% response time of 6 min. The detection limit is estimated at 1 ppm (5 mg/m³) at a signal-to-noise ratio of 5.

The selectivity for organophosphorus compounds of this class of chemical interfaces is found to be promising (maximum 1% of the GB response) although nitrogen dioxide probably damages the chemical interface in the long run. Presently, both the sensitivity and the response time are far from relevant with respect to requirements to be expected for a chemical sensor for nerve agents. Sensitivity may be increased by employing different application techniques as well as higher frequency SAW devices. Chemical adaptation of the chemical structure of the ligand may be used for that purpose as well as to obtain only reversible responses. Modern computation of structure/activity relationships may be of some help to find out the required features of such a ligand

Acknowledgements—The authors wish to thank the following persons, all of the TNO Prins Maurits Laboratory A J Nederlof for experimental assistance, W Duvalois for recording the scanning electron micrographs and performing the EDX analysis and Dr H L Boter for critically reading the manuscript Furthermore, Ing E J M Fakkeldij of Delft University of Technology is acknowledged for performing the XPS measurements and their interpretation

Finally, the Dutch Ministry of Defence is acknowledged for financial support (assignment A88/K/416)

REFERENCES

- M S Nieuwenhuizen, A J Nederlof and A W Barendsz, *Anal Chem*, 1988, **60**, 230
- M S Nieuwenhuizen and A J Nederlof, *Sensors and Actuators*, 1992, **B9**, 171
- A Slobodnik, P H Carr and A J Bureau, *J Appl Phys*, 1973, **44**, 4831
- H Wohltjen and R Dessy, *Anal Chem*, 1979, **51**, 1458
- M S Nieuwenhuizen and A Venema, *Sensors and Materials*, 1989, **1**, 261
- M S Nieuwenhuizen and A Venema, in W Goepel, J Hesse and J N. Zemel (eds), *Sensors A Comprehensive Survey*, Vol 2, p 64 VCH, Weinheim, 1992
- O S Milanko, S A Milinkovic and L V Rajakovic, *Anal Chim Acta*, 1992, **269**, 289
- G G Guilbault, *Anal Chimica Acta*, 1967, **39**, 260
- E P Scheide and G G Guilbault, *Anal Chem*, 1972, **44**, 1764
- W. M Shackelford and G G Guilbault, *Anal Chimica Acta*, 1974, **73**, 383
- G G Guilbault and Y. Tomita, *Anal Chem*, 1980, **52**, 1484
- G. G Guilbault, J Affolter, T Tomita and E S Kolesar, *Anal Chem*, 1981, **53**, 2057
- G G Guilbault, Y Tomita and E S Kolesar, *Sensors and Actuators*, 1981, **2**, 43
- G G Guilbault, J Kristoff and R Owens, *Anal Chem*, 1985, **57**, 1754
- P B Balog, T B Stanford, R J Nordstrom and R C Burgener, AMD Report TR-86-003, 1986
- G. Olofsson, FOA Report C 40142-C1, 1981
- G Olofsson, U Jonsson and S Bergek, *Proc 3rd Conf on Sensors and Actuators*, Philadelphia, 1985, 443
- M J van Sant, Dissertation, Univ New Orleans, 1985
- G G Guilbault, G Lubrano, J Ngeh-Ngwambi, J M Jordan and P H Foley, CRDEC Report CR-87056, 1987
- G G Guilbault and J Ngeh-Ngwambi, *NATO ASI Ser.*, 1988, **C226**, 187
- J Ngeh-Ngwambi, P H Foley, J M Jordan, G G Guilbault and G Palleschi, *Proc 2nd Int Meeting on Chemical Sensors*, Bordeaux, 1986, 515
- J Ngeh-Ngwambi, P H Foley, S S Kuan and G G Guilbault, *J Am Chem Soc*, 1986, **108**, 5444
- H Wohltjen, N L Jarvis, A W Snow, J Giuliani and W R Barger, *Proc Int Symp Protection Against Chemical Warfare*, Stockholm, 1983, 51
- W R Barger, J Giuliani, N L Jarvis, A W Snow and H Wohltjen, *J Env Sci Health*, 1985, **B20**, 359
- H Wohltjen, A W Snow and D S Ballantine, *Proc 3rd Conf on Sensors and Actuators*, Philadelphia, 1985, 66
- W R Barger, H Wohltjen, A W Snow, J Lint and N L Jarvis, *ACS Symposium Series*, 1986, **309**, 155
- J Lint, H Wohltjen, N L Jarvis and A W Snow, *ACS Symposium Series*, 1986, **309**, 309
- D S Ballantine, S L Rose, J W Grate and H Wohltjen, *Anal Chem*, 1986, **58**, 3058
- J W Grate, A W Snow, D S Ballantine, H Wohltjen, M Abraham, R A McGill and P Sasson, *Proc 4th Int Conf on Sensors and Actuators*, Tokyo, 1987, 579
- A W Snow, L G Sprague, R L Soulen, J W. Grate and H Wohltjen, *J Appl Polym Sci*, 1991, **43**, 1659
- A R Katritzky, R J Offerman, J M Aurrecochea and G P Savage, *Talanta*, 1991, **37**, 911
- A R Katritzky, R J Offerman, G P Savage and B Pilarski, *Talanta*, 1991, **37**, 921
- A R Katritzky, G P Savage and B Pilarski, *Talanta*, 1991, **38**, 201
- A R. Katritzky, J N Lam and H M Fajd-Allah, *Talanta*, 1991, **38**, 535
- D M Davis, R E Miller, J A Parsons, A W Snow, L W Sprague, R L Soulen, J W Grate and H Wohltjen, *J Appl Polym Sci*, 1991, **43**, 1659
- L J Kepley, R M Crooks and A J Ricco, *Anal Chem*, 1992, **64**, 3191
- G R van de Berg, H C Beck and H P Benschop, *Bull Environ Contam Toxicol*, 1984, **33**, 505
- T M Ward, I L Alcox and G M Wahl, *Tetrahedron Letters*, 1971, **00**, 4421
- G. G Guilbault and J Das, *J. Phys Chem.*, 1969, **73**, 2243
- G G Guilbault and E P Scheide, *J Inorg Nucl Chem*, 1970, **32**, 2959
- K H Kellmuth and H Mirzai, *Fresenius Z Anal Chem*, 1985, **321**, 224
- A. J Nederlof and M S Nieuwenhuizen, *Rev. Sci Instrum.*, 1993, **64**, 501
- M S Nieuwenhuizen and A. J. Nederlof, unpublished results.