KfK 4661
März 1990

Germanium Determination by Graphite Furnace AAS: Systematic Studies Covering Liquid Sample Introduction as well as Hydride Techniques with In-Situ Concentration

H. O. Haug, C. Ju
Institut für Heiße Chemie

Kernforschungszentrum Karlsruhe

KERNFORSCHUNGSZENTRUM KARLSRUHE

Institut für Heisse Chemie

KfK 4661

GERMANIUM DETERMINATION BY GRAPHITE FURNACE AAS: SYSTEMATIC STUDIES COVERING LIQUID SAMPLE INTRODUCTION AS WELL AS HYDRIDE TECHNIQUES WITH IN-SITU CONCENTRATION

H. O. Haug, C. Ju

Kernforschungszentrum Karlsruhe GmbH, Karlsruhe

Kernforschungszentrum Karlsruhe GmbH
Postfach 3640, 7500 Karlsruhe 1

ISSN 0303-4003

"Germanium Determination by Graphite Furnace AAS: Systematic Studies Covering Liquid Sample Introduction as well as Hydride Techniques with In-Situ Concentration."

ABSTRACT

In the determination of Ge by graphite furnace atomic absorption spectrometry the highest enhancement of the Ge absorbance signals and improved reproducibility were obtained with atomization from the pyrolytic graphite platform using Pd or Pd/Mg nitrate chemical modifiers. The characteristic mass found was about 30 pg Ge/0.0044 A•s for the integrated absorbance signals in nitric acid and in alkaline solutions. A relative standard deviation (RSD) of 1 to 3% was obtained for 1 ng Ge samples. Atomization from the wall of a pyrolytically coated graphite tube resulted generally in a decrease of the Ge signals with the number of firings, and a lower precision.

Hydride generation techniques were combined with the direct introduction of Ge hydride into the graphite furnace and trapping by thermal decomposition. This in-situ deposition of the Ge was achieved after the previous deposit of Pd or Pd/Mg modifier (pretreatment temperature 1100 to 1200 °C) on the pyrolytic graphite platform or on a piece of graphite foil at temperatures of 700 to 800 °C. At a chemical yield of 80 and 90%, respectively, the characteristic mass was about 40 pg Ge/0.0044 A•s. The RSD for 1 ng Ge samples was about 3% for the Pd and 2% for the Pd/Mg modifier. The detection limit was 30 pg Ge in terms of absolute analyte mass and 3 ng Ge/l in terms of concentration in the buffered sample volume (10 ml) of the hydride generator.

"Germanium Bestimmung mittels Graphitrohrofen-AAS: Systematische Untersuchungen mit flüssigen Proben sowie Hydridtechnik mit in-situ Konzentrierung"

ZUSAMMENFASSUNG

Bei der Bestimmung von Ge mit der Graphitrohrofen Atomabsorptionsspektrometrie wurden die höchsten Ge Absorptionssignale und günstige Reproduzierbarkeit bei der Atomisierung von der Pyrographit-Plattform mit Pd- oder Pd/Mg-Nitrat als chemischen Modifier erhalten. Die charakteristische Masse war bei Peakflächenauswertung ca. 30 pg Ge/0.0044 A·s in salpetersauren und in alkalischen Lösungen. Eine relative Standardabweichung (RSD) von 1 bis 3% wurde für Proben mit 1 ng Ge gefunden. Bei Atomisierung von der Wand pyrolytisch beschichteter Graphitrohre ergab sich eine geringere Reproduzierbarkeit und allgemein nahmen die Ge Signale stetig mit der Zahl der Aufheizzyklen ab.

Die Hydridtechnik wurde mit der direkten Einleitung des Ge Hydrids in den Graphitrohrofen und Abscheidung durch thermische Zersetzung kombiniert. Die in-situ Konzentrierung des Ge wurde durch vorherige Aufgabe von Pd oder Pd/Mg Modifier (Vorbehandlungstemperatur 1100 bis 1200 °C) auf der Pyrographit-Plattform oder auf einem gleichgrossen Stück Graphitfolie bei Temperaturen von 700 bis 800 °C erreicht. Bei einer chemischen Ausbeute von 80 bzw. 90% war die charakteristische Masse ca. 40 pg Ge/0.0044 A·s. Die RSD lag für Proben mit 1 ng Ge bei ca. 3% mit Pd und 2% mit Pd/Mg Modifier. Als Nachweisgrenze wurden 30 pg Ge in bezug auf die absolute Analytmasse und 3 ng Ge/l als Konzentration in der gepufferten Analysenlösung (10 ml) des Hydridgenerators gefunden.

TABLE OF CONTENTS

1. INTRODUCTION

The trace analysis of germanium by graphite furnace atomic absorption spectrometry (GF-AAS) may suffer from low sensitivity caused by losses of volatile Ge compounds (GeO or $GeCl_4$ for example) prior to atomization.

D.J. JOHNSON et al. /1/ who first used a graphite furnace as atomizer for Ge attributed the low sensitivity to the formation of GeO(g) prior to atomization. The effect of matrix components were studied by Y. MINO et al. /2/, as well as M. STUDNICKI /3/, and positive interferences on the absorbance of Ge were found for perchloric acid, nitric acid, alkali nitrates, alkali hydroxides, or phosphoric acid, negative effects for hydrochloric and sulfuric acids.

Several authors have discussed the mechanism of GeO formation /2, 4, 5, 6, 7/ during the pretreatment steps. Y. SOHRIN et al. /7/ found evidence that the premature formation of GeO can be prevented by diminishing the reducing activity of the graphite surface by oxidizing acids, such as nitric or perchloric acid, in the sample solution; and by keeping the analyte as germanate(IV) in alkali hydroxide solutions /2, 4, 5/. The high enhancement of the Ge absorbance signals by the addition of sodium hydroxide /2/ was used for a sensitive analysis, yielding a characteristic mass of 40 pg/0.0044 A. Ge was lost from Na_2GeO_3 as GeO at temperatures higher than 830 °C from 0.1 M NaOH /4/ and about 1050 °C from 0.5 M NaOH /2/. The formation of the GeO was measured by A. KOLB et al. /5/ and by NI CHE MING et al. /6/ by the molecular absorption at 265.9 nm in the temperature range of about 900 to 1400 °C.

K. DITTRICH et al. /8/ found a high improvement in the Ge sensitivity by some metal nitrates, especially by Ni or Ba nitrate solutions at 0.1 M concentration. Ashing temperatures up to 1200 °C were possible using these nitrates as chemical modifiers. It was explained by the stabilizing effect of the nitrate ion on tetravalent Ge and the formation of thermally stable germanates ($MGeO_3$, M = divalent metal). The characteristic mass was 17 and 25 pg Ge/0.0044 A, respectively.

In acidic media containing hydrobromic acid the Ge may be completely lost as $GeBr_4$ during the drying and pretreatment steps. After neutralization with NaOH and addition of Ba nitrate modifier, K. DITTRICH et al. /8/ found only a slightly depressed Ge signal caused by the bromide content (characteristic mass 43 pg Ge/0.0044 A).

G.R. CARNRICK and W.B. BARNETT /9/ used Mg nitrate as chemical modifier and platform atomization. The best results were obtained using a cool-down step in which the graphite tube cooled to ambient temperature between the pretreatment step and the atomizing step. With 1.5 ng Ge in aqueous solution and 50 ug $Mg(NO_3)_2$ a characteristic mass of 30 pg Ge/0.0044 A.s was found.

In a systematic study we have investigated the application of palladium nitrate or mixed palladium and magnesium nitrate modifiers for the GF-AAS of Ge, because these modifiers were very effectively used /10, 11, 12/ to stabilize in the pretreatment step many elements, including for example the main group elements Sn and Pb, at several hundred degrees higher than possible with other methods. Hence it could be expected to volatilize $NaCl/NaNO_3$ salts by the pretreatment steps, the salts being formed during neutralization of strong hydrochloric acid solutions. Such analyses were required from investigations within the project GALLEX (the international experiment for measuring solar neutrinos) on Ge adsorption and desorption on glass and other surface materials. Another effective chemical separation from matrix components is provided by the hydride generation technique.

The determination of germanium by generation of the volatile covalent hydride using sodium tetrahydroborate(III) was introduced by E.N. POLLOCK and S.J. WEST /13/ and by F.J. FERNANDEZ /14/ in 1973. M. THOMPSON et al. /15/ found a distinct maximum of the analytical signals of Ge and Sn at about 0.1 M HCl and similar results were obtained with other acids.

Frequently, the hydride generation was combined with the direct transfer of the germane (GeH_4) into the atomizer, e.g. a graphite furnace in AAS by T. INUI et al. /16/. Considerable improvements in concentration detection limits were achieved through preconcentration when the hydride generation was coupled to the hydride collection in a liquid nitrogen cooled trap as used by E.J. KNUDSON and G.D. CHRISTIAN /17/ in combination with a graphite furnace. When the separation of several species was desired a chromatographic column was coupled between the liquid nitrogen trap and the atomization cell. In graphite furnace AAS, M.O. ANDREAE et al. /18/ and G.A. HAMBRICK et al. /19/ have swept GeH_4 and methyl-germanium species, respectively, by an inert carrier gas into the graphite tube which was preheated to the atomization temperature of 2600 °C /18/, or 2700 °C /19/.

Also effective for the preconcentration of the gaseous hydrides has been the use of a graphite furnace both for the hydride trapping and as atomization cell. The trapping made use of the thermal decomposition of the hydrides in the graphite tube which was preheated to the optimum decomposition temperature of the particular hydride followed by the atomizing step.
G. DRASCH et al. /20/ introduced AsH_3 into the graphite tube at 850 °C via an axial glas tubing; R.E. STURGEON et al. /21/ used the internal purge gas line for trapping As and Se which were transported by the generated hydrogen and the Ar carrier gas.

Further improvements in this method of hydride generation and trapping in the graphite furnace was achieved by the introduction of the volatile hydride and carrier gas via the sample introduction port into the preheated graphite tube. R.E. STURGEON and coworkers used this technique for the in-situ concentration and determination of As and Se /21, 22, 23/. In the measurement of tin by decomposition of SnH_4, in addition, use was made of the Pd modifier in the graphite tube /24/. After the experimental part of our work was finished, we got notice of the paper by F.S. DOIDGE et al. /35/ using the technique of thermal trapping of the Ge on the graphite tube wall applying also the Pd modifier.

In the present work the possibilities were studied for using the hydride generation in measuring trace concentrations of Ge in the given medium concentrated hydrochloric acid media, combined with an easy way of adapting the hydride generator to the graphite furnace for Ge in-situ concentration by thermal trapping of the hydride on the more effective pyrographite platform after applying a suitable chemical modifier.

2. EXPERIMENTAL

2.1 Instrumentation and Parameters

Instrumental and graphite furnace conditions for the measurement of germanium are given in Table 1. New graphite tubes and platforms were used in the studies of Ge atomization as a function of the pyrolysis temperature with liquid samples or the decomposition temperature with hydride sample introduction, respectively. Tubes and platforms were also replaced after about 180 firings in case of the measurement of the reproducibility of the Ge signals.

The temperature programs for drying, decomposing, and atomizing from the tube wall or the platform are summarized in Table 2.

Table 1 Instrumentation

SpectrAA-40 atomic absorption spectrometer (Varian Techtron, Australia)
GTA-96 graphite furnace with programmable sample dispenser
Continuous degassing of the dispenser rinse solution before entering the syringe by an On-line Degasser ERC-3120 (ERMA Optical Works Inc., Tokyo) to prevent formation of troublesome gas bubbles in the syringe

Ge hollow cathode lamp, current 5 mA
Wave length 265.2 nm (slit 1.0 nm)
Deuterium lamp for background compensation

Pyrolytically coated graphite tubes (Part Nr. 63-100002-00)
Pyrolytic graphite platforms (12.5 x 2.5 x 1 mm, Part Nr. 63-100004-00) or Graphite foil (12 x 4 x 0.4 mm; Ringsdorff Werke GmbH, Bonn-Bad Godesberg, FRG) with larger surface area due to its fibrous structure

Ar gas flow in the graphite furnace generally 3 L/min for drying, pyrolysis, and cleaning steps, with gas stop at atomization; 0.2 L/min Ar during GeH4 introduction and thermal deposition step

Sample volume generally 10 uL;
Palladium nitrate modifier: 5 ug Pd in 5 uL volume, or
Palladium/Magnesium nitrate modifier: 15 ug Pd + 10 ug $Mg(NO_3)_2$ (same masses in 15 uL with pre-injected modifier mode, resp.)

Table 2 Thermal parameters in wall and platform atomization applying Pd or Pd/Mg modifier for aqueous samples, and for Ge deposition from the hydride, respectively

steps	temperature [°C]					ramp [s]	hold [s]
	liquid samples			GeH4 decomposition			
				pre-inj. modifier			
	wall	platform	pre-inj. modifier platform	wall	platform		
injection	25	25	25	25	25		
drying	90	90	90	90	90	1	–
	120	140	140	120	140	50	–
	250	250	250	250	250	20	–
pyrolysis/ pretreatment	1100 |	1200 |	1200	1100	1200	10	20
sample intr.	| |	| |	step 1	800	800	5	150
gas-stop	1100	1200	1200	1100	1200	–	2
atomization	2600	2700	2700	2600	2700	0	3
cleaning	2700	2700	2700	2700	2700	–	5
cooling		40	40		40	14	8

2.2 Reagents

Germanium Stock Solution

A commercially available Ge standard (Alfa Products-Ventron, Danvers, MA, USA) with a Ge concentration of 1000 ug Ge/mL in 2% KOH solution was diluted with deionized water (18 MOhm specific resistance) to a working stock solution of 10 ug Ge/mL (molar ratio of K:Ge = 26). Further dilutions usually containing 100 ng Ge/mL were then prepared with the media investigated and were stored in polyethylene bottles up to 5 days.

Chemicals

The chemicals used were of 'suprapure' quality (Merck, Darmstadt, FRG) or at least of analytical reagent grade.

Palladium nitrate solution was prepared /10/ by dissolving Pd metal powder (Alfa Products, 99.998% purity) in a few mL of concentrated nitric acid and dilution to 6 g Pd/L using deionized water. Magnesium nitrate solution was prepared by dissolution of $Mg(NO_3)_2 \times 6H_2O$ (Merck, suprapure) in water.

The Pd nitrate modifier /25/ and the mixed Pd and Mg nitrate modifier /10/ solutions were obtained by further dilution of appropriate aliquots and applied as specified in Table 1.

For hydride generation a 2 to 4% m/vol sodium tetrahydroborate(III) solution was freshly prepared by dissolving $NaBH_4$ (Merck, Darmstadt, FRG) in 0.005 M NaOH solution. The solution was kept only for one day.

A 0.1 M acetate buffer at pH 4.0 has been chosen as the weakly acidic medium for the germane (GeH_4) generation by the $NaBH_4$ reaction.

2.3 Hydride Generator

Two types of hydride generator techniques were applied, i.e. a batch type system and a continuous hydride generator to demonstrate the in-situ collection and concentration of the Ge by decomposition of the GeH_4 inside the graphite tube. The batch type generator was used in most of the experiments.

2.3.1 Batch-Type Hydride Generator

The batch-type hydride generator was similar to that described by J. PIWONKA et al. /26/ consisting of a tapered glass reaction vessel with a T-shaped carrier gas and borohydride solution feed. Details are summarised in Table 3 and are shown in Fig. 1.

Table 3 Batch-type hydride generator

Tapered glass reaction vessel
Volume 10 to 20 mL, or 100 mL, resp.
Low volume cap with gas/liquid separator
Vessel and cap joined by standard taper with PTFE sleeve
Introduction of Ar carrier gas and $NaBH_4$ solution through a T-connector via a submerged PTFE tubing
Feed-through connections of the PTFE tubings by O-ring sealed PTFE reducing unions
PTFE capillary connecting generator and graphite furnace
Quartz capillary for GeH_4 introduction into the graphite tube

Sample aliquot added to acetate buffer solution (pH=4)
Ar carrier gas flow 50 to 100 mL/min
Metering of 2 to 4 % $NaBH_4$ solution with peristaltic pump

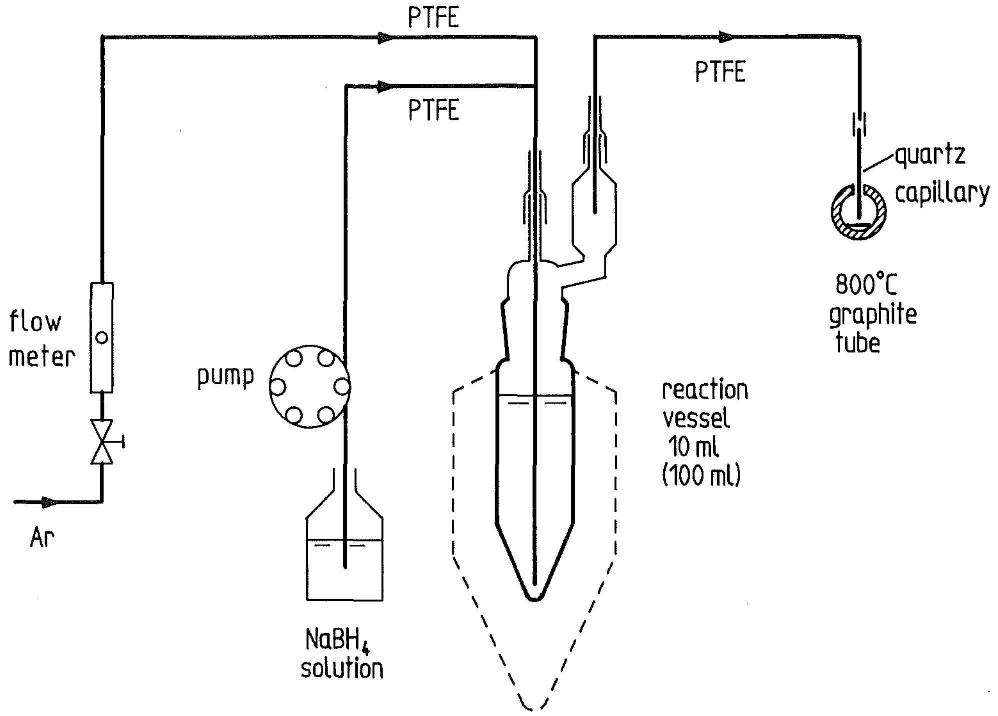

Fig. 1 Principle of the hydride generator used for GeH$_4$ introduction into the graphite furnace

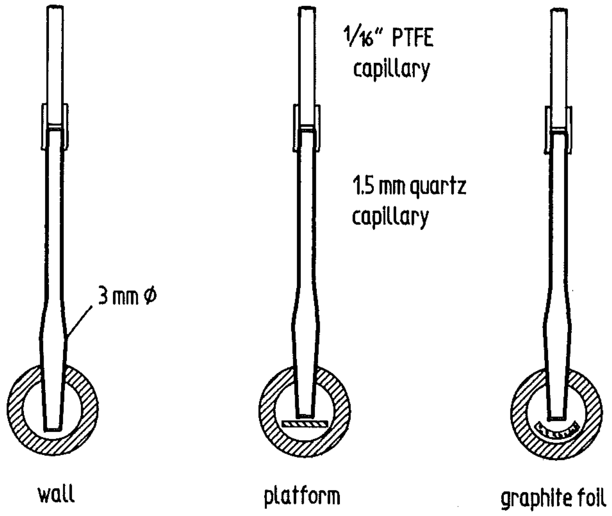

Fig. 2 Introduction of gaseous hydride and carrier gas mixture into the preheated graphite tube via a conical quartz tubing placed next to the modifier treated surface

2.3.2 Continuous Hydride Generator

A continuous hydride generator similar to the construction by YAMAMOTO et al. /27/ was used in the course of this study. The data on the continuous hydride generator are summarized in Table 4.

Because the reaction for generating the GeH_4 with sodium borohydride is practically instantaneous, the reaction volume of the coiled PTFE tubing corresponding to a reaction time of about 10 sec was sufficient. The important feature of the reaction coil is the complete stripping of the hydride from the liquid into the carrier gas /28/.

The collection time in the graphite furnace was about 3 min for the 10 mL sample volume. Because of the cyclic operation of the application and pretreatment of the modifier prior to the introduction and the atomization of the Ge in the graphite furnace, the overall operation remains discontinuous.

Table 4 Continuous hydride generator

Reaction coil 50 cm of 1/8" PTFE tubing
4-Channel peristaltic pump
Fixed volume (e.g. 10 mL) of acetate buffer solution (pH=4) containing the analyte introduced at 4 mL/min (channel 1) via a 4-way valve, switched to acetate buffer solution at 2 mL/min (channel 2) following the analyte/buffer solution
0.7% $NaBH_4$ solution at 1 mL/min (channel 3)
Ar gas metered at 1 to 2 mL/min through the fourth channel
Gas/liquid separator at end of reaction coil
Ar carrier gas flow of 50 to 100 mL/min fed into gas/liquid separator
PTFE capillary connecting generator and graphite furnace
Quartz capillary for GeH_4 introduction into the graphite tube

3. RESULTS AND DISCUSSION

The temperature dependence of the Ge absorbance signals was studied for the methods of pretreatment and atomizing from

- the wall of the pyrolytically coated graphite tube,
- the pyrolytic graphite platform,
- the platform with a cool-down step between the pretreatment and the atomizing step /9/,
- liquid sample introduction with added modifier,
- pre-injected modifier and liquid sample introduction,
- pre-injected modifier and Ge hydride sample introduction.

The effect of the pyrolysis temperatures was measured in the range between 300 °C and the maximum temperature characterized by a steep decrease of the Ge signals at further temperature increase. The maximum useful pyrolysis temperature was considered to be about 50 degrees below that distinct decline.

Signal enhancement by the different modifiers were compared to the methods of absorbance measurements in absence of a modifier, the latter being shown in Fig. 3. With wall atomization and at pyrolysis temperatures higher than 600 °C the observed decrease of the Ge signal indicated losses of Ge due to the formation of volatile GeO during the decomposition of Ge compounds and the possible reduction by the hot carbon surface /5/.

3.1 Liquid Sample Introduction with Added Modifier

3.1.1 Study of the Ge Signals with Wall Atomization

Table 5 shows that the Ge signals from aqueous Ge solutions (water or 0.1 M HNO_3) with atomization from the wall of a pyrocoated graphite tube have been strongly enhanced using the Mg nitrate (Fig. 4), Pd nitrate (Fig. 5), and Pd/Mg nitrate modifier (Fig. 6), resp., as compared to the case without a modifier. These results indicate a significant extension of the range of possible pyrolysis temperatures to about 900, 1150, and 1150 °C, resp.. The time-resolved peakform of the Ge absorbance signals was a narrow peak with no tailing and little background (Fig. 7).

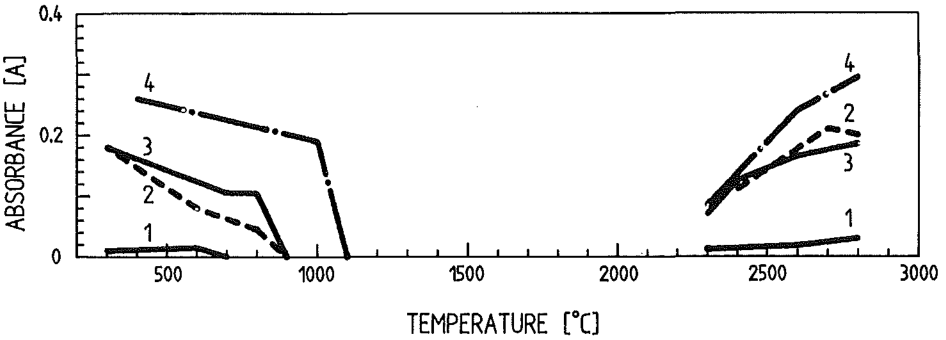

Fig. 3 Effect of pretreatment and atomizing temperatures on the Ge absorbance signal from 1 ng Ge in absence of a chemical modifier:
(1) tube wall (water); (2) platform (water);
(3) platform/cool-down step (water or 0.1 M HNO_3);
(4) platform/cool-down step (0.1 M NaOH)

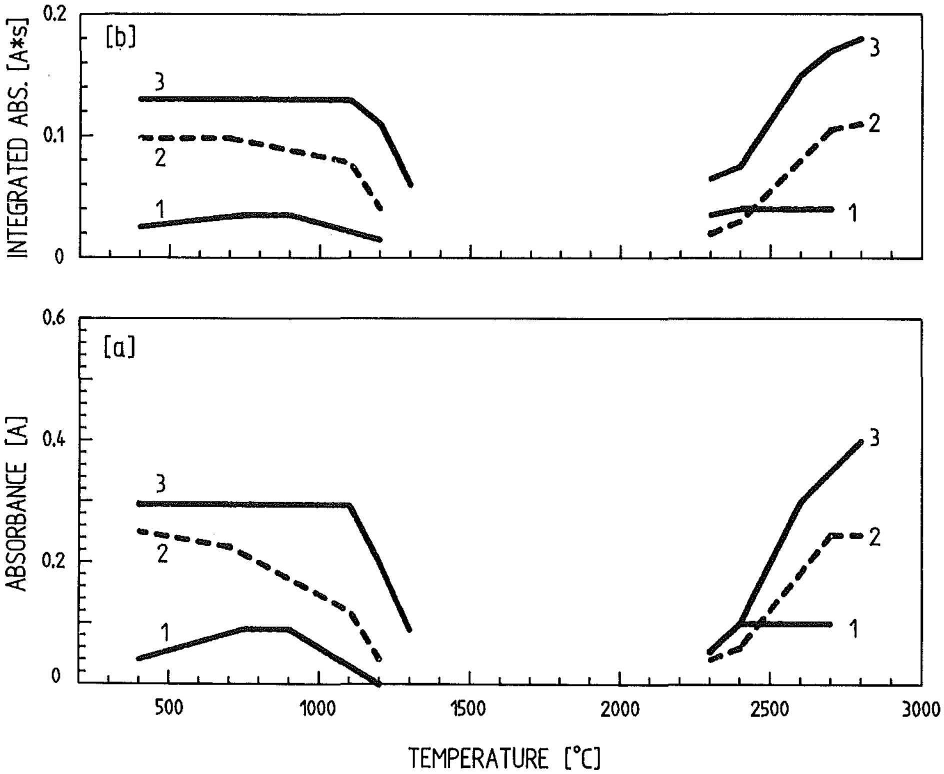

Fig. 4 Effect of pretreatment and atomizing temperatures on the Ge signal from 1 ng Ge in water with 8 ug Mg modifier: [a] peak-height mode; [b] peak-area mode; (1) tube wall; (2) platform; (3) platform/cool-down step

The optimum atomization temperature (for the same pyrolysis temperature of 400 °C without modifier, 600 °C with Mg, and 1000 °C with Pd or Pd/Mg modifier) was found to be in the range 2400 to 2500 °C.

In 0.1 M sodium hydroxide solutions the possible pretreatment temperatures are 1250 to 1300 °C with both the Pd modifiers. Increasing the concentration from 0.1 to 1.0 M NaOH caused an increase of the Ge integrated absorbance signal by a factor of two in the case of Pd modifier, but had no such effect on the measurement with Pd/Mg modifier.

3.1.2 Study of the Ge Signals with Platform Atomization

Nitric Acid Solutions

Atomization of aqueous Ge from a pyrolytic graphite platform produced a delay in the appearance time, and in the absence of a modifier the sensitivity was increased considerably, relative to wall atomization (Table 5). This is to be expected /8, 9/ due to volatilization of the Ge species into an atmosphere of higher temperatures which promotes greater dissociation and atomization of Ge. The use of Mg, Pd, or Pd/Mg modifiers produced a further increase in signal (Table 5).

The platform atomization with an intermediate cool-down step to 100 °C before the atomization step combined with a very fast heating rate of 2000 °C/sec was introduced for the measurement of Ge by G.R. CARNRICK et al. /9/ using a Mg nitrate modifier. While the method resulted in an increased Ge signal in case of the Mg modifier little effect was noted with the palladium modifiers, compared to normal platform atomization.

The maximum useful pyrolysis temperatures increased to approximately 1200 to 1250 °C for the platform methods using the Pd or Pd/Mg modifier for Ge in water or 0.1 M HNO_3 solutions.

The optimum atomization temperature for these conditions was found to be 2600 to 2700 °C using integrated absorbance measurements.

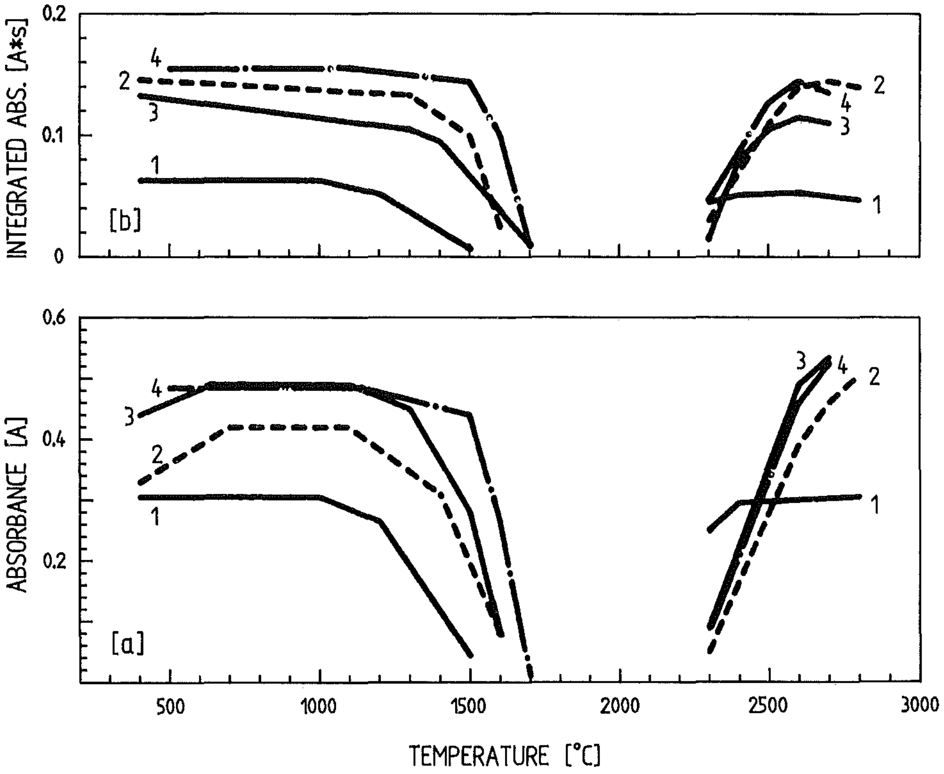

Fig. 5 Effect of pretreatment and atomizing temperatures on the Ge signal from 1 ng Ge with 5 ug Pd modifier:
[a] peak height mode; [b] peak area mode;
(1) tube wall (water or 0.1 M HNO_3 or 0.1 M NaOH);
(2) platform (water or 0.1 M HNO_3); (3) platform/ cool-down step (water); (4) platform (0.15 M NaOH)

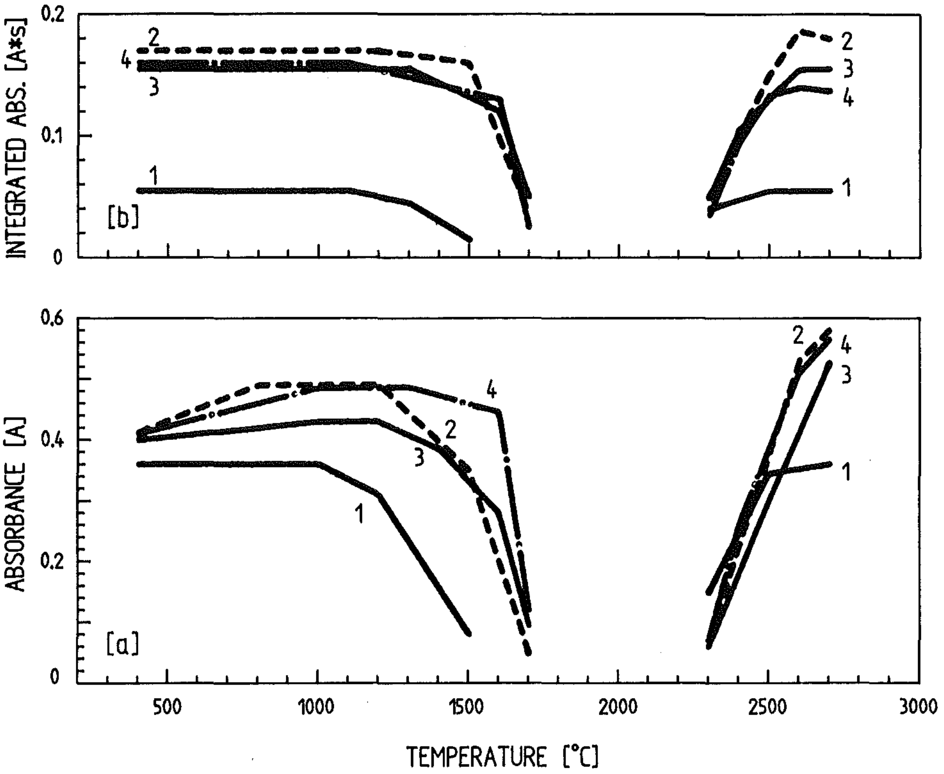

Fig. 6 Effect of pretreatment and atomization temperatures on the Ge signal from 1 ng Ge using Pd/Mg modifier: [a] peak height mode; [b] peak area mode; (1) tube wall (0.1 M HNO_3); (2) platform (water or 0.1 M HNO_3); (3) platform, cool-down step (water or 0.1 M HNO_3); (4) platform (0.1 M NaOH)

Time-resolved Ge Signals

The time-resolved peakform showed a complex structure towards the lower pyrolysis temperatures in absence of a modifier or with the Mg modifier. This behaviour suggests that more than one Ge species were involved in the dissociation and atomization process. However, in platform atomization with the cool-down step using Mg modifier, a single peak was observed for pyrolysis temperatures between 300 and 1100 °C. This is probably due to atomization occurring under the more stable temperature conditions that are obtained using the cool-down step prior to atomization. There may perhaps be a timely coincidence of the dissociation and atomization of two species or the preferential occurence of one atomization mechanism.

The peakform of the Ge absorbance signals using Pd or Pd/Mg modifier and platform atomization was a narrow single peak returning quickly to the base line (Fig. 7).

Alkaline Solutions

In 0.1 M NaOH solution, the Ge measurement with platform atomization and cool-down step resulted in the highest signal in the absence of a modifier, and a pyrolysis temperature as high as 950 °C could be used (Table 5). Ge(IV) has been stabilized as Na_2GeO_3 suppressing its premature reduction by the graphite during the pyrolysis steps /2, 5, 7/. The peakform was a steeply rising, single peak.

Using the Mg modifier, a complex peak resulted from alkaline solution up to 0.1 M NaOH which deteriorated the peak height mode. At higher than 0.1 M NaOH a strong increase of the background signal which coincided with the Ge peak limited useful measurements.

Using Pd or Pd/Mg modifier on the platform, the peakform of the Ge absorbance signals from 0.1 M NaOH solution showed minor differences to the signals from optimized conditions for water or nitric acid solutions. Pyrolysis temperatures of 1250 to 1300 °C are possible, allowing a good separation of many matrix components. If the NaOH concentration was increased from 0.1 to 1.0 M the Ge signals remained essentially constant, but the excess of strong alkali caused a drastic reduction of the lifetime of the graphite tubes and platforms.

Table 5 Parameter study with different modifiers mixed with the sample (1 ng Ge)
(useful atomization temp.: wall 2500 to 2600 °C,
platform 2600 to 2700 °C)

MEDIA		WALL	PLATFORM normal	PLATFORM cool-down	REMARKS
WITHOUT MODIFIER:					
HNO_3 (H_2O)	max. pyrolysis temp. [°C]	600	(750)	750	
	peak-form (*), type	N	C	C	
	charact. mass [pg], p. height	300	55	35	p.t. 600 °C
	peak area	400	70	80	
NaOH	max. pyrolysis temp. [°C]	–	–	950	
	peak-form (*), type	–	–	N	
	charact. mass [pg], p. height	–	–	20	p.t. 800 °C
	peak area	–	–	60	
Mg NITRATE MODIFIER:					
HNO_3 (H_2O)	max. pyrolysis temp. [°C]	900	(1000)	1050	
	peak-form (*), type	N	N	N	
	charact. mass [pg], p. height	50	22	16	p.t. 600 °C
	peak area	130	44	34	
	reproducib. [% RSD] p. height	–	–	2-5	
NaOH	peak-form (*), type	C	C	C	strong
		no useful	measurements		background
Pd NITRATE MODIFIER: (*)					
HNO_3 (H_2O)	max. pyrolysis temp. [°C]	1150	1200	1200	
	charact. mass [pg], p. height	16	10	10	p.t. 1100 °C
	peak area	70	32	39	
H_2O	reproducib. [% RSD] p. height	(5-12)@	1-4	2-5	
HNO_3	p. height	(3-5)@	2-5	1-4	
NaOH	max. pyrolysis temp. [°C]	1250	1200	1200	
	charact. mass [pg], p. height	18	9	9	p.t. 1100 °C
	peak area	70	28	30	
	reproducib. [% RSD] p. height	(5-11)@	3-7	2-6	
	peak area		2-3		
Pd/Mg NITRATE MODIFIER: (*)					
HNO_3 (H_2O)	max. pyrolysis temp. [°C]	1150	1250	1250	
	charact. mass [pg], p. height	12	10	10	p.t. 1100 °C
	peak area	80	26	29	
	reproducib. [% RSD] p. height	(3-11)@	1-5	2-5	
	peak area		1-3		
NaOH	max. pyrolysis temp. [°C]	1300	1250	1250	
	charact. mass [pg], p. height	15	9	9	p.t. 1100 °C
	peak area	60	28	31	
	reproducib. [% RSD] p. height	(3-8)@	4-7	5-10	
	peak area		1-3		

'p.t.' = pyrolysis temperature

*) The Ge signal was normally a narrow peak with fast return to the baseline (= N); deviations are specified as complex (= C).

@) Decreasing signals with number of firings in wall atomization.

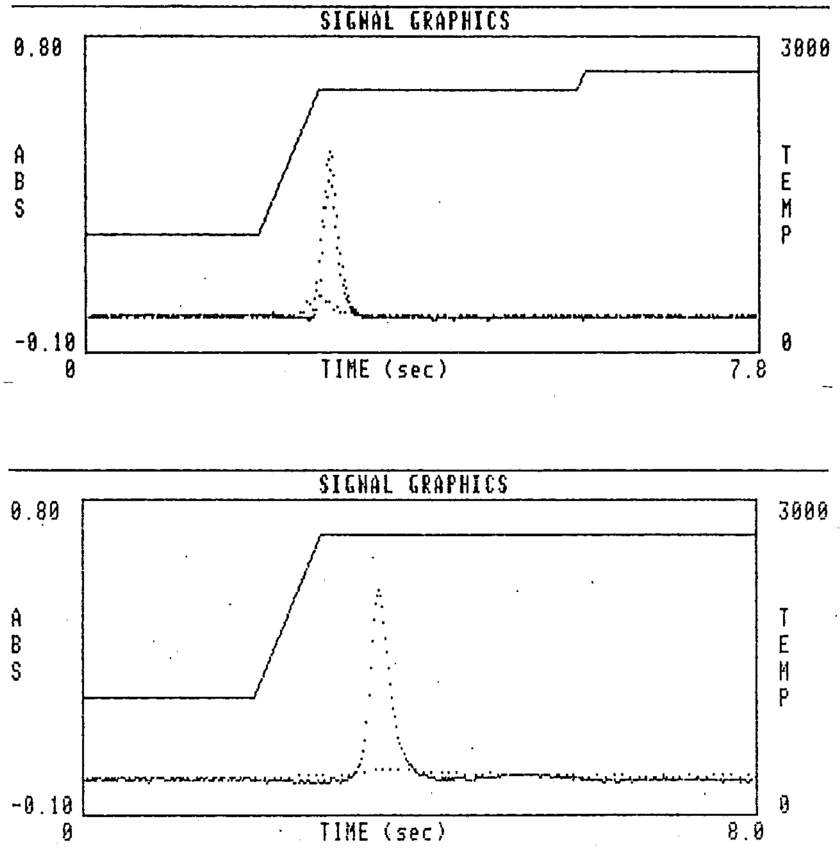

Fig. 7 Time-resolved peakforms of the Ge absorbance and background signals (pyrolysis temperature 1100 °C):
top, wall atomization 2500 °C;
bottom, platform atomization 2700 °C.

Ge in Weakly Basic Sodium Chloride Solutions

For determining Ge in hydrochloric acid solutions it was thought that Ge may be lost as the volatile tetrachloride during the drying and pyrolysis temperature programme. Therefore, hydrochloric acid solutions were first neutralized and a small excess of up to 0.1 M NaOH added (taking into account the acid of the modifier solution).

At pyrolysis temperatures below 1000 °C, the Ge signals were accompanied by a large background signal which disappeared at 1050 °C or higher temperatures. In Fig. 8 it is indicated that pyrolysis temperatures up to 1250 °C could be selected with platform atomization using either the Pd nitrate or the Pd/Mg nitrate modifier.

Calibration and Analysis of Samples

In the analysis of synthetic solutions of Ge in weakly basic sodium chloride solutions, pyrolysis temperatures of 1100 to 1200 °C and platform atomization were applied. The calibration curve was linear up to about 0.18 A.s for peak area mode (and 0.7 A for peak heights, resp.), in case of both the Pd or Pd/Mg modifiers.

Since part of the samples contained gallium trichloride in strong hydrochloric acid solution, they were neutralized and the interference of Ga on the Ge response studied in the concentration range of 1 to 300 ug Ga/mL in 0.5 m NaCl + 0.1 M NaOH solutions. A decrease of the Ge integrated absorbance signals was found only for Ga concentrations higher than 100 or 200 ug Ga/mL for the Pd or Pd/Mg modifier, respectively. the precision of the Ge integrated absorbance values for 1 ng Ge samples was 1 to 3% RSD.

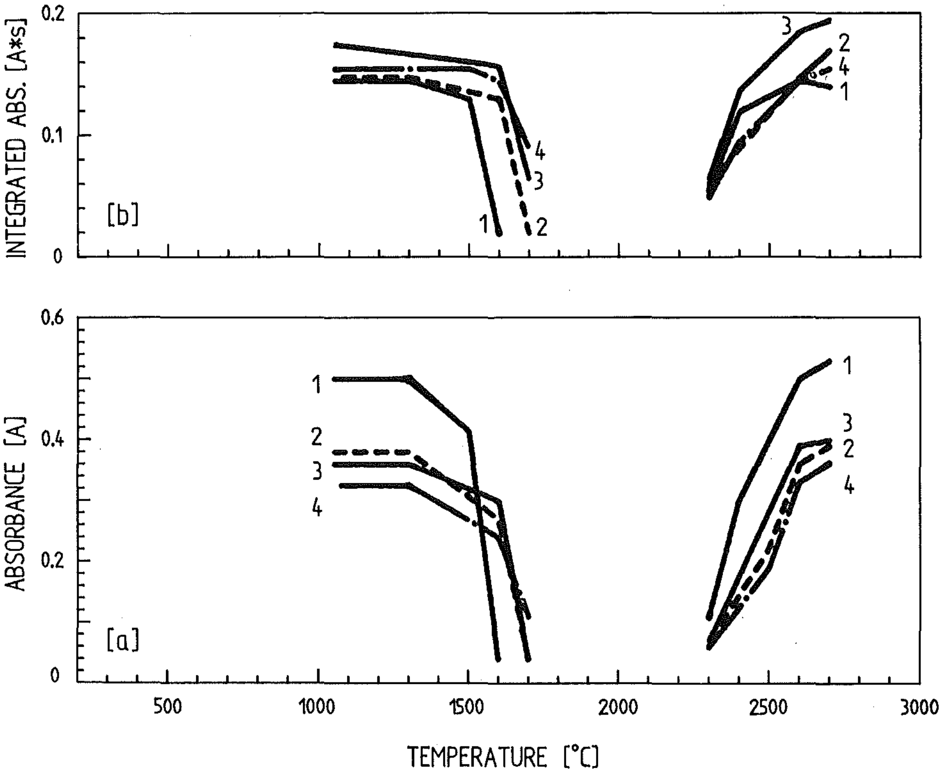

Fig. 8 Effect of pretreatment and atomization temperature on the Ge signal from 1 ng Ge in alkaline NaCl and $GaCl_3$/NaCl solutions:
[a] peak height mode; [b] peak area mode;
(1) platform, 0.5 M NaCl/0.1 M NaOH solution, Pd modifier, and (2) Pd/Mg modifier; (3) platform, 100 ppm $GaCl_3$/0.5 M NaCl/0.1 M NaOH solution, Pd modifier, and (4) Pd/Mg modifier.

3.2 Liquid Sample Introduction Applying Pre-injected Modifier

Pre-injecting the chemical modifier prior to injecting the sample, and using the same pretreatment temperature as the pyrolysis temperature was examined. The results are shown in Fig. 9 and in Table 6.

With atomization from the wall of a pyrocoated graphite tube the Ge signals indicate a possible pretreatment and pyrolysis temperature of 1100 °C for the Pd and the Pd/Mg modifier. The time-resolved Ge signal was a narrow peak accompanied by a noticable background absorption signal.

Table 6 Comparative study of the Ge absorption signals using different pre-injected modifiers and liquid sample introduction (1 ng Ge)
(useful atomization temp.: wall 2500 to 2600 °C,
platform 2600 to 2700 °C)

MEDIA		WALL	PLATFORM		REMARKS
			normal	cool-down	
Mg NITRATE MODIFIER:					
H_2O	max. pyrolysis temp.# [°C]	950	950	-	
	charact. mass [pg], p. height	66	18	-	p.t. 800 °C
	peak area	240	40	-	
Pd NITRATE MODIFIER:					
H_2O	max. pyrolysis temp.# [°C]	1050	1200	1200	
	charact. mass [pg], p. height	11	9	8	p.t. 1000 °C
	peak area	73	26	30	
	reproducib. [% RSD] p. height	(3-7)@	2-4	2-3	
Pd/Mg NITRATE MODIFIER:					
H_2O	max. pyrolysis temp.# [°C]	1100	1250	1250	
	charact. mass [pg], p. height	11	10	8	p.t. 1100 °C
	peak area	34	25	30	
	reproducib. [% RSD] p. height	(3-11)@	2-4	2-3	
	peak area		1-3		

#) Pretreatment temperature for the pre-injected modifier was the same as the pyrolysis temperature ('p.t.') of the sample.

@) Decreasing signals with the number of firings in wall atomization.

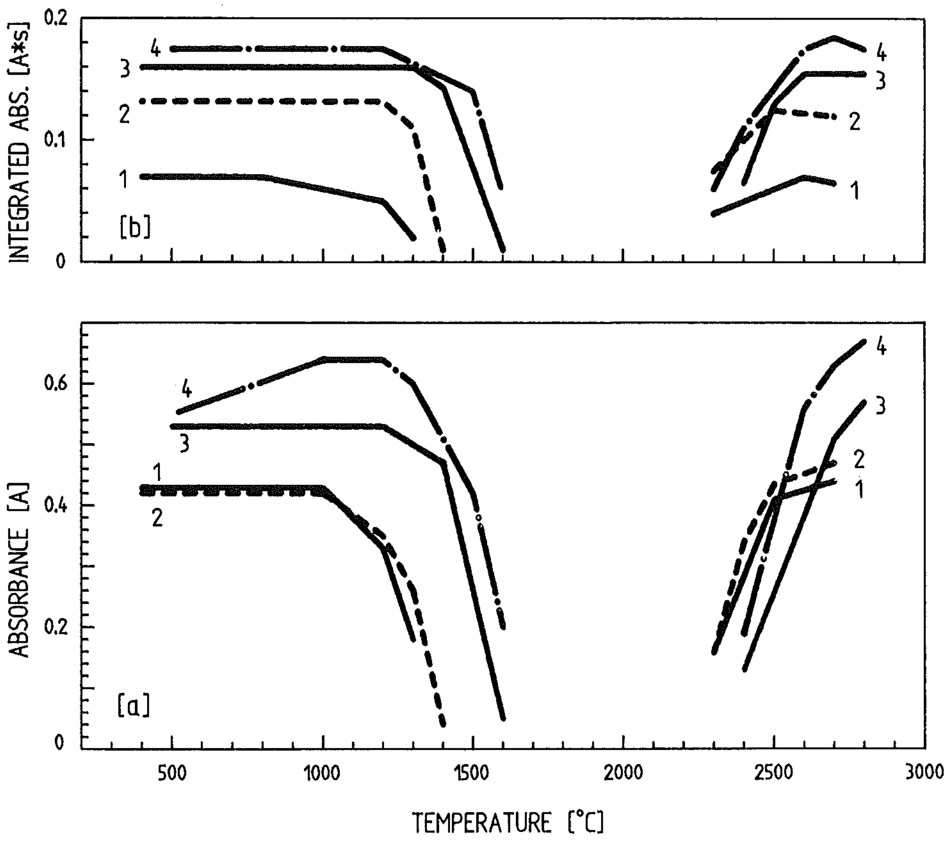

Fig. 9 Effect of pretreatment and atomizing temperatures on the Ge signal from 1 ng Ge in 10 uL aqueous sample with pre-injected Pd or Pd/Mg modifier: [a] peak height mode; [b] peak area mode; (1) tube wall, Pd modifier; (2) tube wall, Pd/Mg modifier; (3) platform, Pd modifier (atomization 2700 °C); (4) platform, Pd/Mg modifier (2700 °C)

With atomization from the pyrolytic graphite platform the Ge signals were considerably enhanced compared to wall atomization, especially in the case of the Pd/Mg modifier. The pyrolysis temperatures could be extended to 1200 °C. The narrow peakform of the time-resolved Ge signals now had a negligible background signal.

3.3 Reproducibility Tests

Relatively high variations of the peak height values (sometimes of more than 10%) of the Ge absorption signals have rather frequently been observed in particular series and repetitive measurements during the course of these investigations on the GF-AAS of Ge. The atomization efficiency is certainly affected by the chemical matrix, the surface conditions of the graphite, the distribution and chemical form of the modifier.

Replicate determinations were performed and the precision has been included in Tables 5 and 6, expressed as the range of the relative standard deviation (RSD) of each successive 5 measurements.

With wall atomization of Ge in solutions using the Pd or the Pd/Mg modifier it is important to note that common to all media (HNO_3, water, NaOH) the Ge signals gradually decreased with the number of heating cycles, especially in alkaline solutions. With pre-injected Pd or Pd/Mg modifiers a similar behaviour was registered which is illustrated in Fig. 10.

The precision improved considerably with Ge atomization from the platform. Applying the Pd or Pd/Mg modifiers to the solutions, essentially constant Ge absorbance signals were found over 160 firings. The best precision was obtained for the integrated absorbance signals of Ge (RSD 1 to 3%).

Also using pre-injected modifier on the platform, the precision of the Ge absorbance and especially the integrated absorbance measurements (RSD 1 to 3%; Fig. 10) has improved considerably compared to wall atomization and the signals were quite constant over about 180 firings.

Effects of aging due to alterations of the tube surface were described for refractory elements by M. HOENIG et al. /29/. L.M. VOTH-BEACH and D.E. SHRADER /30/ have related some properties of Pd as chemical modifier to the physical form of the Pd, however, they observed also non-reproducible results due to differences in the graphite tube surfaces. Hence, little is known about alterations of the surface conditions by aging, or possibly other parameters which might affect Ge more than other elements.

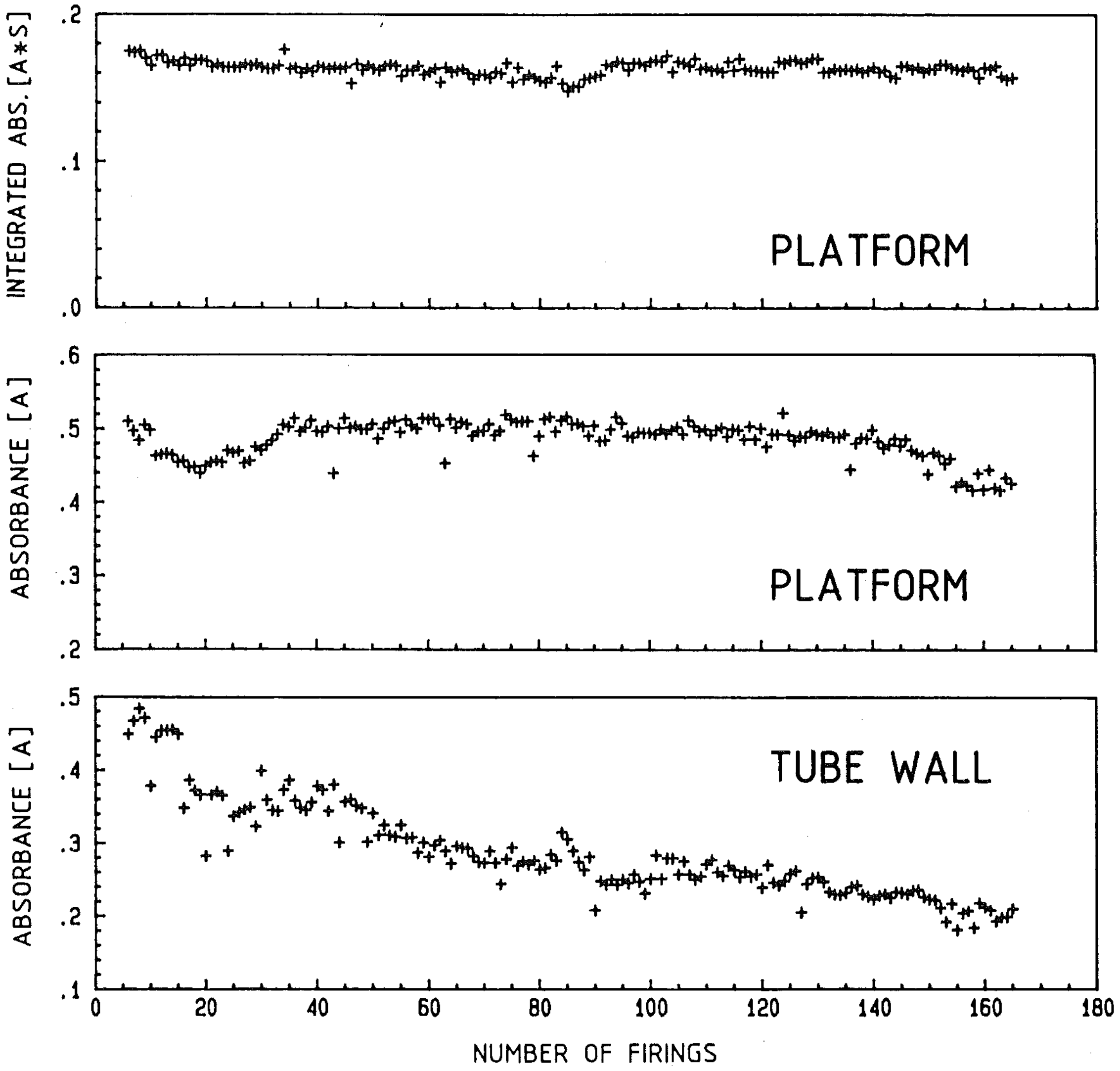

Fig. 10 Reproducibility of the Ge absorbance and integrated absorbance signals of 1 ng Ge samples in water with pre-injected Pd/Mg modifier

3.4 Germanium Hydride Sample Introduction

3.4.1 Hydride Generation

Effects of Acidity in Germane Generation

Germane is formed in good yield by the reaction of Ge(IV) in acidic aqueous solution (pH < 8) with borohydride ion, BH_4^-, according to:

$$H_2GeO_3 + BH_4^- + H^+ \longrightarrow GeH_4 + H_3BO_3$$

A large excess of borohydride is necessary in this reaction and most of the borohydride is hydrolysed in acidic medium forming hydrogen gas:

$$BH_4^- + H^+ + 3\ H_2O \longrightarrow H_3BO_3 + 4\ H_2(g)$$

From the rate law of this borohydride decomposition reaction J. AGTERDENBOS and D. BAX /28/ deduced the halflife of the borohydride to be about 0.04, 4.3, and 430 milliseconds at pH 2, 4, and 6, respectively. The hydride formation reaction is a fast reaction and must be complete before a considerable portion of the reagent has decomposed.

The borohydride solution acts as a base shifting the pH to higher values than initial. The relative narrow range of acid concentration for a maximum yield in the germane generation /15, 31/ in the acid near-neutral pH range requires the control of the pH by buffered solutions /18, 19/. J.R. CASTILLO et al. /32/ and L. HALICZ /33/ found the optimum medium for the GeH_4 generation in 0.1 M acetic acid-sodium acetate solution at pH 4 to 5. In the present work this acetic acid/acetate buffer at pH=4 was selected.

$NaBH_4$ Solution Concentration

For maximum GeH_4 response a reagent concentration of 2% m/vol $NaBH_4$ was chosen to provide a convenient volume of reagent addition by the peristaltic pump to the 10 to 20 mL reaction vessel over a period of about 60 to 100 sec in order to keep the evolved hydrogen gas flow rate low and evenly distributed. For the 100 mL vessel the $NaBH_4$ concentration had to be increased to 4% m/vol or higher.

Reaction and Stripping Time

GeH_4 has no acidic properties and is insoluble in aqueous solutions. M.O. ANDREAE and P.N. FROELICH /18/ determined the time required for the conversion of Ge(IV) in solution to the hydride, for the separation of the gaseous hydride from the liquid phase, and for the transport of the hydride into the atomizer. The maximum response was reported to be reached at a time which was considered as practically identical with the deadspace flushing time of the generator. Due to the low head-space of the generator used in this work, further stripping for about 1 min after the end of the $NaBH_4$ addition was sufficient.

3.4.2 Procedure of Ge In-situ Collection in the Graphite Furnace

The germanium hydride was introduced into the preheated graphite furnace and the Ge collected and in-situ concentrated by thermal decomposition of the GeH_4 prior to atomization.

The Ar carrier gas flow was used to displace the air from the reaction vessel before the reaction was started, and further to strip the generated Ge hydride and hydrogen gas from the buffer solution and the head-space of the hydride generator. The end of the PTFE transfer capillary tubing was connected to a quartz capillary, about 5 cm in length and 1.5 mm outer diameter.

After the automatic dispensing of the modifier solution and the end of the drying and heating cycle (pretreatment temperature 1100 to 1200 °C) for the Pd nitrate or mixed Pd/Mg nitrate modifier, the graphite tube was heated to the optimum decomposition temperature of about 800 °C. The Ar gas flow in the graphite furnace was reduced to 0.2 L/min and the quartz capillary inserted into the normal sample introduction port. The end of the capillary was placed close either to the wall opposite the sample hole or the surface of an inserted platform or graphite foil, respectively, where the modifier has been deposited. As indicated in Fig. 2 the tip of the quartz capillary had a conical shape with its larger diameter being 2.5 to 3 mm, thus it came to a rest when inserted into the 2 mm wide hole of the graphite tube (simultaneously closing the sample introduction port in the graphite tube).

The peristaltic pump was started and during a period of about 1 min a volume of 2 to 2.5 mL sodium borohydride solution was pumped through a T-connector of PE via the submerged Ar carrier gas line into the buffer solution containing the analyte sample.

Thus, a relatively even gas evolution was obtained. After the $NaBH_4$ addition the reaction vessel was flushed with Ar for about 1 min more, then the capillary was removed from the graphite tube. After flushing the graphite furnace with Ar for a few seconds, the usual atomization step followed with gas stop.

Altogether, the total sequence of atomizer steps is controlled by the spectrometer, except the quartz capillary for the introduction of the hydride which has to be placed into and removed from the graphite tube by hand at the programmed times.

3.4.3 Trapping of Ge by Decomposition of the Hydride in the Graphite Furnace

The deposition of the Ge analyte in the graphite furnace by decomposition of germane requires the previous deposit of a suitable modifier, and thus is very similar to the Ge measurement from liquid samples using the pre-injected modifier. Because of the better response of the Ge measurements with platform atomization, the Ge collection in the graphite furnace was primarily studied on a pyrolytic platform.

The GeH_4 was introduced through a quartz capillary ending closely to the hot surface of the platform where the GeH_4 was thermally decomposed. The platform was previously contacted with Pd nitrate or mixed Pd/Mg nitrate solution and heated to a pretreatment temperature of 1100 to 1200 °C.

The effect of the decomposition temperature on the Ge signals is shown in Fig. 11. Germane is effectively decomposed and trapped on the particular modifier-treated surface over a temperature range of 300 to 1000 °C and atomization temperatures of 2700 °C were sufficient. Early work by J.H. MUELLER and N.H. SMITH /34/ stated the thermal decomposition of GeH_4 begins at 340 to 360 °C. However, on a Pd treated surface the decomposition of GeH_4 starts below 300 °C. Routinely, the temperature for collecting the Ge on the platform was choosen 700 to 800 °C.

Because the decomposition of the GeH_4 is a heterogeneous gas/solid surface reaction a piece of graphite foil with its larger surface of fibrous material was inserted into the graphite tube instead of a platform. A higher absorbance signal was observed as shown in Fig. 11.

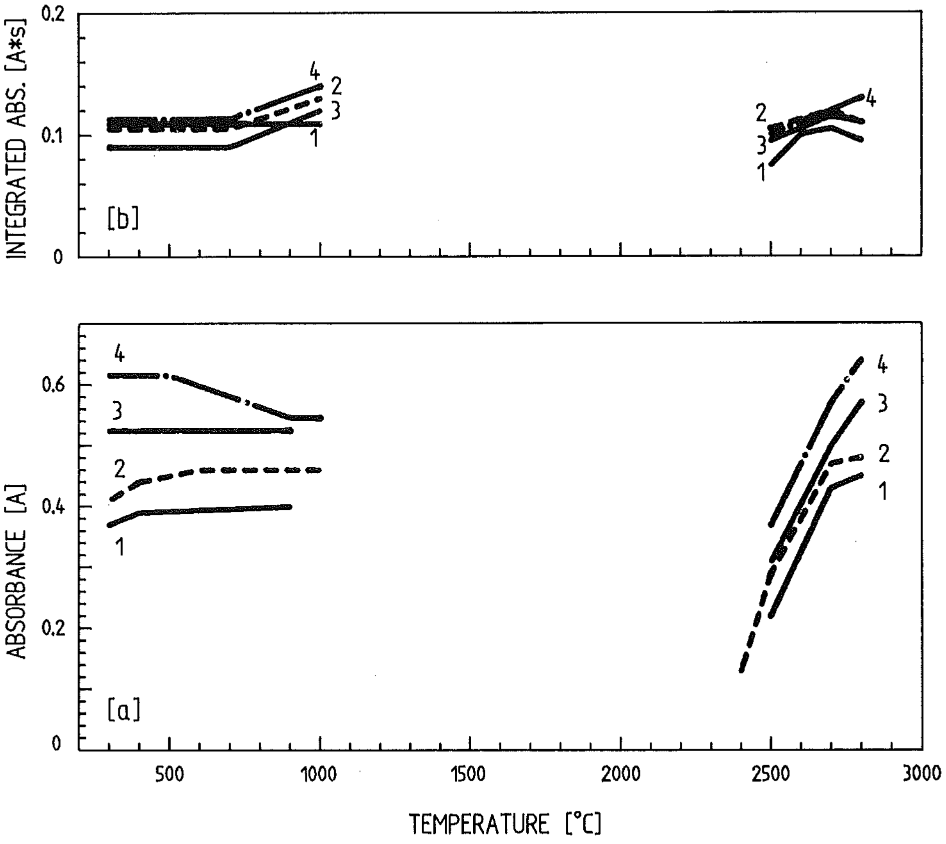

Fig. 11 Hydride generation of 1 ng Ge and effect of GeH_4 decomposition and atomization temperatures on the Ge signals with pre-injected Pd or Pd/Mg modifiers: [a] peak height mode; [b] peak area mode;
platform: (1) Pd, (2) Pd/Mg modifier;
graphite foil: (3) Pd, (4) Pd/Mg modifier

An average Ge recovery of about 80 % with Pd/Mg modifier was evaluated from the Ge signals obtained by atomization of the Ge from the platform, where it was thermally trapped from the GeH_4 which was generated from 1 ng Ge added to the buffer solution, i.e. the Ge signal was 80% of the response of 1 ng Ge introduced into the furnace in a 10 uL volume of aqueous solution. A recovery of about 90% with Pd modifier was found when a piece of graphite foil was used instead of the platform.

The evolved gases and the Ar carrier gas flow from the hydride generator were passed directly through the PTFE transfer line between the generator and the graphite furnace tube. No influence of water vapor in the carrier gas on the deposition of Ge was found, thus a drying tube did not seem to be necessary.

Table 7 Comparative study of the Ge absorption signals using Pd or Pd/Mg pre-injected modifiers and GeH_4 sample introduction and thermal deposition (1 ng Ge)
(useful atomization temp.: wall 2600 °C,
platform 2600 to 2700 °C)

MEDIA		WALL	PLATFORM	GRAPHITE FOIL
Pd NITRATE MODIFIER:				
modifier pretreatment temp.	[°C]	1100	1200	1200
GeH_4	decomposition temp. [°C]	800	800	800
	charact. mass [pg], p. height	20	11	9
	peak area	60	40	44
	reproducib. [% RSD] p. height	–	3	–
	peak area	–	3–7	–
Pd/Mg NITRATE MODIFIER:				
modifier pretreatment temp.	[°C]	1100	1200	1200
GeH_4	decomposition temp. [°C]	800	800	800
	charact. mass [pg], p. height	16	10	8
	peak area	55	38	37
	reproducib. [% RSD] p. height	5–7	2	–
	peak area	–	2	–

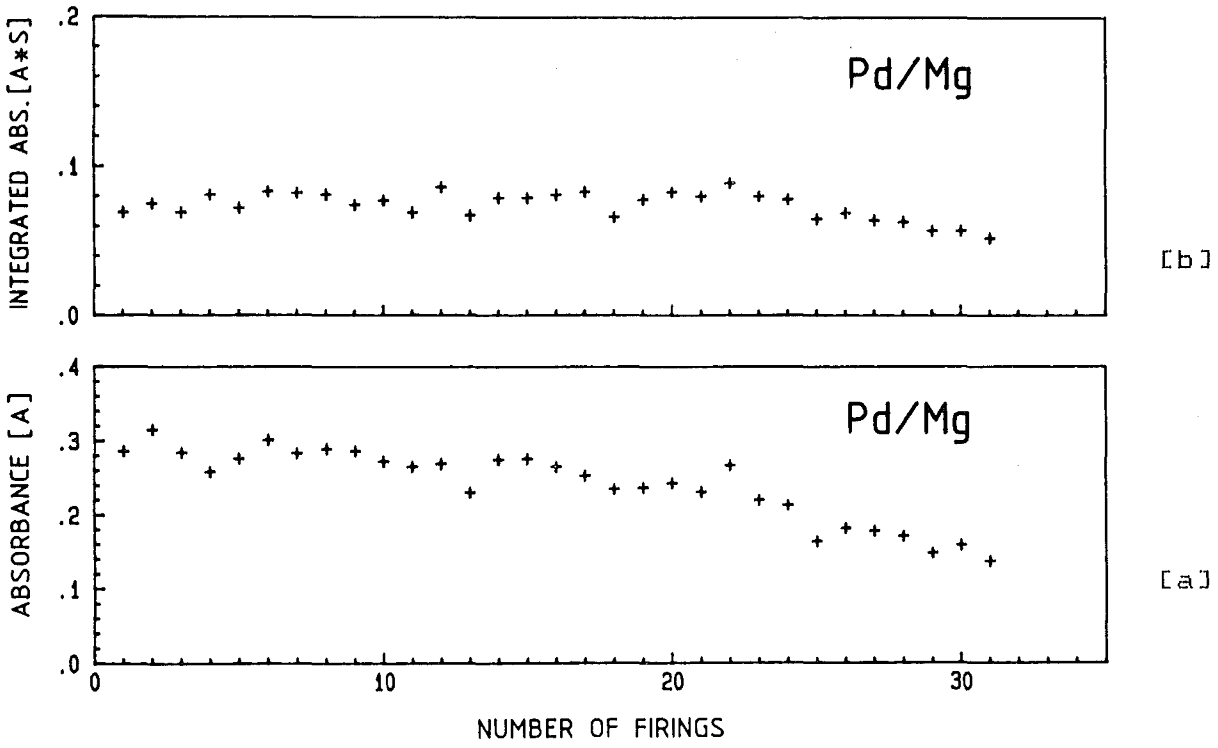

Fig. 12 Reproducibility of Ge measurements after hydride generation from 1 ng Ge samples, decomposition and atomization on the graphite tube wall using pre-injected Pd/Mg modifier:
[a] peak height mode; [b] peak area mode

3.4.4 Reproducibility of the Ge Hydride Signal Response

The precision of the Ge measurement with hydride generation and decomposition in the graphite furnace was studied for the deposition on the platform in comparison to the tube wall. The RSDs of the Ge absorbance and integrated absorbance signals are included in Table 7. Again it is important to note that fairly rapidly decreasing signals (50% after 30 firings) were recorded for wall atomization with aging of the graphite tube, as is illustrated in Fig. 12, thus, supporting the same observation as in Fig. 10 for aqueous samples.

P.S. DOIDGE et al. described in their paper /35/ a continuous GeH_4 generation and a similar technique of direct deposition of Ge by thermal decomposition on the graphite tube wall. These authors confirmed our observations of rather high relative standard deviations with wall atomization of Ge, and found a decreasing precision during aging of the graphite tube.

Clearly, the precision has been improved considerably in our measurements using the in-situ concentration on a platform or a graphite foil with the Pd as well as the Pd/Mg modifier, and applies both in the peak height and in the peak area mode (see Table 7). Good precision of about 2 % RSD (for each 5 successive measurements) resulted with the Pd/Mg modifier (Fig. 13). A large number of heating cycles (>60) with reasonably constant signals were possible using platform atomization.

3.4.5 Detection Limits

A characteristic mass of 40 pg Ge/0.0044 A.s for the integrated absorbance (10 pg Ge/0.0044 A for peak absorbance) was obtained with the platform. Detection limits were determined at very low Ge concentrations (100, 20, 10 pg Ge added to 10 mL buffer solution), and values of about 30 pg Ge (3 sigma, n=10) were found in terms of an absolute analyte mass applying the Pd or Pd/Mg modifiers. A detection limit of 3 ng Ge/L in terms of concentration related to the sample + buffer volume (10 mL) in the hydride generator was obtained.

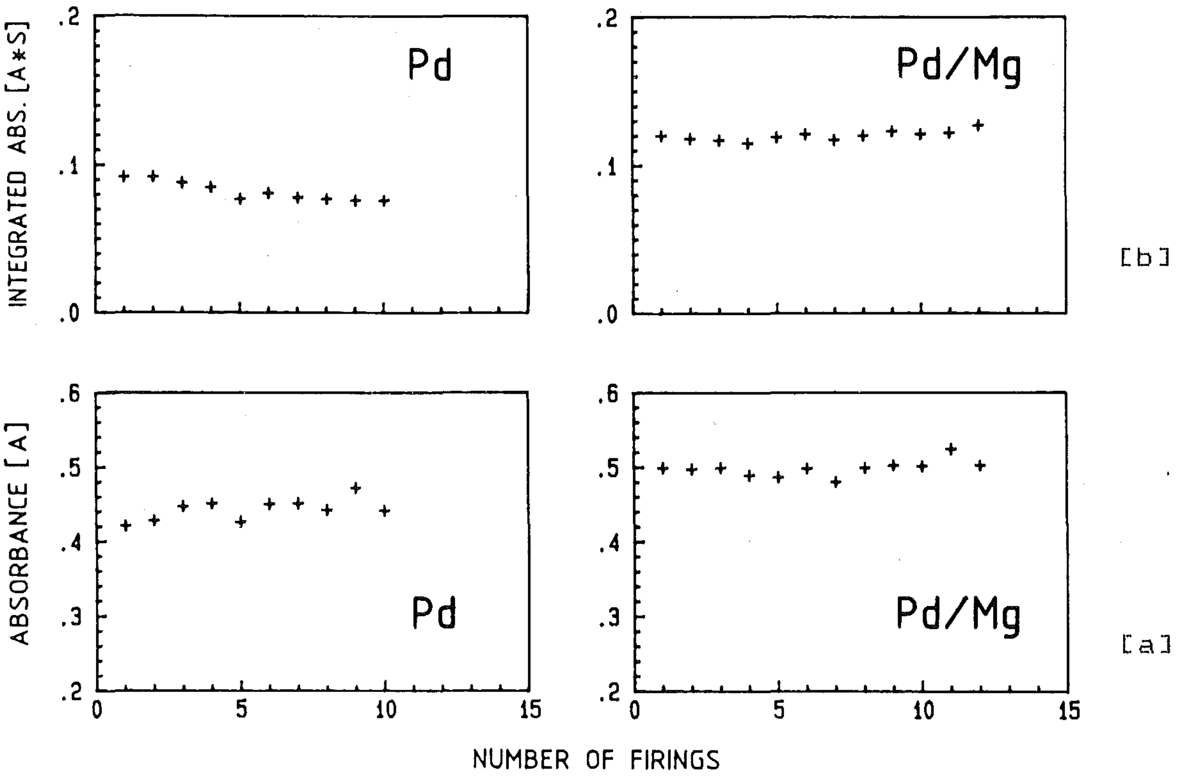

Fig. 13 Reproducibility of Ge measurement after hydride generation from 1 ng Ge samples, decomposition and atomization on a graphite platform using pre-injected modifier:
[a] peak height mode; [b] peak area mode;

3.4.6 Calibration and Analysis of Samples

The response of the Ge absorbance signal for thermal trapping on the platform was linear to about 0.17 A.s for the peak area mode (and 0.7 A for peak heights, respectively). Synthetic solutions (from the Ge sorption/desorption experiments) were analysed which contained <100 ng Ge/mL and about 2 orders of magnitude higher concentrations of gallium in NaCl/NaOH solutions. Interference of Ga in the GeH_4 generation could be compensated by increasing the $NaBH_4$ concentration. Thus, with 4 to 5% m/vol $NaBH_4$ no interference was observed at less than 100 ug Ga/mL buffered solution. As shown in Fig. 14, the Ge response decreased at higher Ga concentrations.

Samples containing 6.6 to 66 ng Ge/mL and 2.75 mg Ga/mL in NaCl solutions, were diluted by a factor of 10 to 100 and analysed directly against solution standards of 0.2 to 1.0 ng Ge. Measurement of recovery gave values of 98 to 109%.

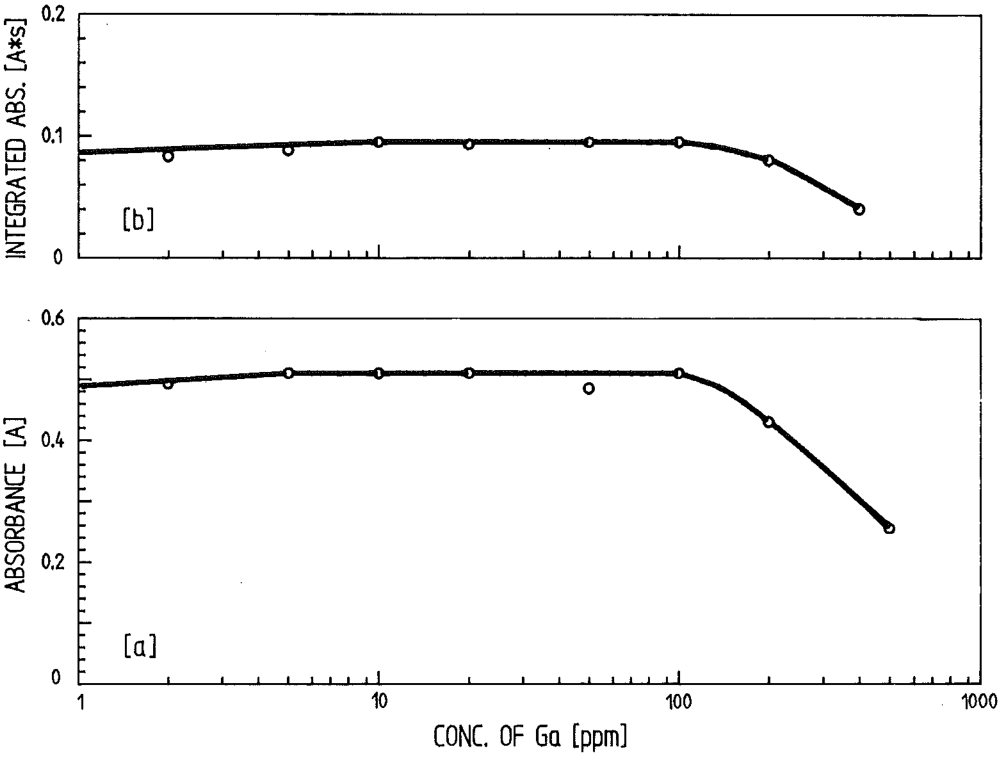

Fig. 14 Effect of Ga concentration on the signal of 1 ng Ge during hydride generation followed by in-situ measurement using pre-injected Pd/Mg modifier: [a] peak height mode; [b] peak area mode

4. CONCLUSION

A high response for the germanium absorbance measurements was obtained in graphite furnace AAS when palladium or mixed palladium/magnesium modifiers were applied in dilute nitric acid or slightly alkaline solutions.

Atomization from the wall of pyrocoated graphite tubes resulted in moderate signals from dilute nitric acid solutions and a higher response for the weakly alkaline solutions. Wall atomization with sample introduction either as a liquid or as GeH_4 with thermal Ge deposition was accompanied by a high relative standard deviation, and the signals decreased gradually with the ageing of the graphite tubes even at rather low numbers of firings.

With platform atomization the Ge signal heights and the possible pyrolysis temperatures increased significantly. Improved reproducibility of the Ge measurements was obtained, with the best precision for the integrated absorbance signals. The number of firings with reasonably constant signals usually extended beyond 200.

Thus, from our experience the recommended procedure for Ge in solutions is platform atomization, with pyrolysis temperatures of 1100 to 1200 °C after application of Pd or Pd/Mg modifier either mixed to the sample or in the pre-injected mode, and signal integration. With hydride generation good precision is obtained by in-situ concentration of the Ge on a platform or a graphite foil with pre-injected Pd/Mg (or Pd) modifier.

The reasons and mechanisms for the high relative standard deviations in the Ge measurements in graphite furnace AAS with the palladium modifiers and the effect during ageing of the graphite tubes and platforms are not understood yet, and further investigations are needed.

5. REFERENCES

/1/ D.J. JOHNSON, T.S. WEST, R.M.DAGNALL
Anal. Chim. Acta 67 (1973) 79-87

/2/ Y. MINO, S. SHIMOMURA
Anal. Chim. Acta 107 (1979) 253-259

/3/ M. STUDNICKI
Anal. Chem. 52 (1980) 1762-1764

/4/ W. WENDL
Fresenius Z. Anal. Chem. 323 (1986) 726-729

/5/ A. KOLB, G. MUELLER-VOGT, W. WENDL, W. STOEBEL
Spectrochim. Acta 42B (1987) 951-957

/6/ NI ZHE-MING, SHAN XIAO-QUAN
Spectrochim. Acta 42B (1987) 937-949

/7/ Y. SOHRIN, K. ISSHIKI, T. KUWAMOTO
Talanta 34 (1987) 341-344

/8/ K. DITTRICH, R. MANDRY, W. MOTHES, J.G. JUDELEVIC
Analyst 110 (1985) 169-175

/9/ G.R. CARNRICK, W.B. BARNETT
Atomic Spectrosc. 5 (1984) 213-214

/10/ G. SCHLEMMER, B. WELZ
Spectochim. Acta 41B (1986) 1157-1165

/11/ G. SCHLEMMER, J.R. MUDAKAVI, B. WELZ
Proc. 4th Coll. Atomspectrom. Spurenanal., Konstanz
6.-9. April 1987, p. 137-151

/12/ L.M. VOTH-BEACH, D.E. SHRADER
Spectroscopy 1 (10) (1986) 49-59

/13/ E.N. POLLOCK, S.J. WEST
At. Absorp. Newslet. 12 (1973) 6-12

/14/ F.J. FERNANDEZ
At. Abs. Newsl. 12 (4) (1973) 93-97

/15/ M. THOMPSON, B. PAHLAVANPOUR
Anal. Chim. Acta 109 (1979) 251-258

/16/ T. INUI, S. TERADA, H. TAMURA, N. ICHINOSE
Fresenius Z. Anal. Chem. 315 (1983) 598-601

/17/ E.J. KNUDSON, G.D. CHRISTIAN
Anal. Lett. 6 (1973) 1039-1054

/18/ M.O. ANDREAE, P.N. FROELICH
Anal. Chem. 53 (1981) 287-291

/19/ G.A. HAMBRICK, P.N. FROELICH, M.O. ANDREAE, B.L. LEWIS
Anal. Chem. 56 (1984) 421-424

/20/ G. DRASCH, L. von MEYER, G. KAUERT
Fresenius Z. Anal. Chem. 304 (1980) 141-142

/21/ R.E. STURGEON, S.N. WILLIE, S.S. BERMAN
Fresenius Z. Anal. Chem. 323 (1986) 788-792

/22/ R.E. STURGEON, S.N. WILLIE, S.S. BERMAN
J. Anal. At. Spectrom. 1 (1986) 115-118

/23/ S.N. WILLIE, R.E. STURGEON, S.S. BERMAN
Anal. Chem. 58 (1986) 1140-1143

/24/ R.E. STURGEON, S.N. WILLIE, S.S. BERMAN
Anal. Chem. 59 (1987) 2441-2446

/25/ L. BEACH
Spectroscopy 2 (12) (1987) 21-23

/26/ J. PIWONKA, G. KAISER, G. TOELG
Fresenius Z. Anal. Chem. 321 (1985) 225-234

/27/ M. YAMAMOTO, M. YASUDA, Y. YAMAMOTO
Anal. Chem. 57 (1985) 1382-1385

/28/ J. AGTERDENBOS, D. BAX
Anal. Chim. Acta 188 (1986) 127-135

/29/ M. HOENIG, F. DEHAIRS, A.M. de KERSABIEC
J. Anal. At. Spectrom. 1 (1986) 449-52

/30/ L.M. VOTH-BEACH, D.E. SHRADER
J. Anal. At. Spectrom. 2 (1987) 45-50

/31/ R.S. BRAMAN, M.A. TOMPKINS
Anal. Chem. 50 (1978) 1088-1093

/32/ J.R. CASTILLO, J. LANAJA, J. AZNAREZ
Analyst 107 (1982) 89-95

/33/ L. HALICZ
Analyst 110 (1985) 943-946

/34/ J.H. MUELLER, N.H. SMITH
J. Am. Chem. Soc. 44 (1922) 1912

/35/ P.S. DOIDGE, B.T. STURMAN, T.M. RETTBERG
J. Anal. At. Spectrom. 4 (1989) 251-5

Appendix A

Improved Performance of the Automatic Sample Dispenser in Graphite Furnace AAS by Continuous Degassing of the Dispenser Liquid

Abstract

The continuous degassing of the dispenser rinse solution has resulted in the improved performance of the automatic sample dispenser in graphite furnace AAS. The formation of troublesome gas bubbles in the dispenser syringe which eventually might lead to dispensing errors, is thus avoided.

Modern computer controlled instruments for graphite furnace atomic absorption spectrometry are frequently equipped with a programmable automatic sample dispensing system.

In the programmable sample dispenser of the Varian GTA-96 graphite furnace (Varian Techtron, Melbourne, Australia) a microcomputer controlled syringe executes the sequence of programmed volumes of blank, modifier, standard, and sample solutions. These solutions which are separated by a slug of air, are taken up in a PTFE capillary tubing, fixed at the dispenser arm. Experience in many laboratories has shown that troublesome gas bubbles were formed in the syringe during normal operation within a relative short time, sometimes within a few hours, thus making a frequent cleaning of the syringe necessary.

Standard Operation

The flow of the rinse solution (deionized water or very dilute acid) through the stepper motor-driven syringe and the PTFE capillary is supported by a 1.2 to 1.5 bar Ar pressure on top of the liquid level in the attached solution delivery bottle. Consequently, the rinse solution which normally is air-saturated anyway, gets over-saturated by dissolved Ar gas. During rinse operation or the liquid take-up into the dispenser capillary, the suction stroke of the syringe causes a reduced pressure in the rinse solution filling the syringe. Reduced pressure necessarily leads to a degassing of liquids, and thus slowly leads to the formation of gas bubbles at the wall of the syringe, and after several hours, as the bubbles are growing, eventually dispensing errors may result.

Effect of Degassing the Sample Dispenser Rinse Solution

The formation of the troublesome gas bubbles in the syringe was completely eliminated by continuously degassing the rinse solution before it enters the syringe. This was achieved, as outlined schematically in Fig. 1, by passing the solution through a gas-permeable tubular PTFE membrane in a vacuum chamber (On-line Degasser ERC-3000 Series, ERMA Inc., Tokyo) connected between the bottle and the syringe.

The only change at the automatic sample dispenser has been to replace the PTFE capillary tubing between the rinse solution bottle and the solenoid valve by a pair of longer capillary tubings form the bottle to the degasser unit and from there back to the valve.

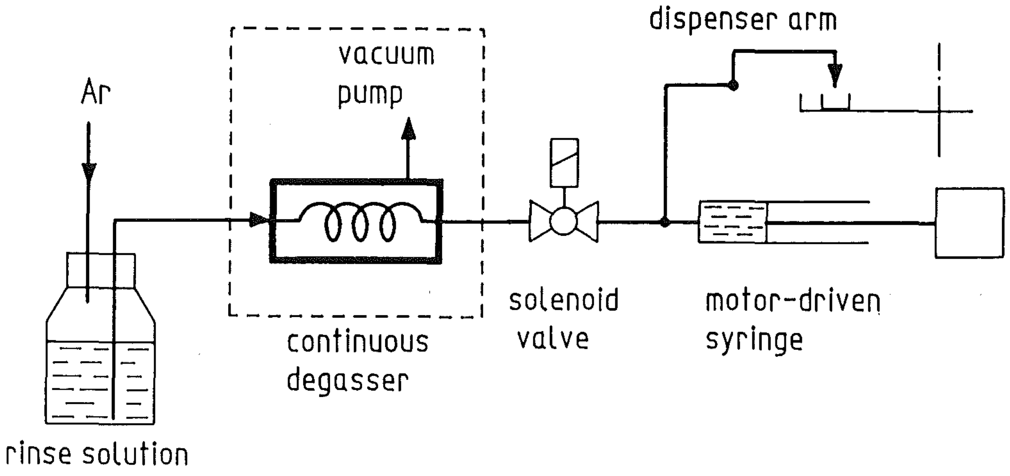

Fig. 1 Avoiding gas bubbles in the syringe by degassing of the dispenser rinse solution

Experience in our laboratory has shown that after introduction of the continuous degassing of the rinse solution no gas bubble in the syringe has been observed within two years of operation. The system was free of additional maintenance.

Conclusion

The introduction of continuous degassing of the dispenser rinse solution resulted in the considerable improvement of the automatic sample dispenser in GF-AAS. Avoiding dispensing errors due to the formation of troublesome gas bubbles, has proven very valuable in routine analysis of a large number of samples and for automatic runs over night.