Determination of traces of sodium and potassium in gallium arsenide by graphite furnace atomic absorption spectrometry and flame atomic emission spectrometry

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Gallium arsenide samples were analyzed for traces of Na and K by graphite furnace atomic absorption spectrometry (GFAAS) and flame atomic emission spectrometry (FAES). The sample was dissolved in hydrochloric acid and bromine. For the GFAAS method the sample matrix need not be removed. The detection limit ($3s$) was found to be $w = 10^{-8}$ For the FAES method the sample matrix was extracted as chlorides with butyl acetate or tributyl phosphate. The detection limit was $w = 3 \times 10^{-8}$ The reproducibility of the results was 3—5 % (GFAAS) and 5—10 % (FAES), respectively.

Gallium arsenide (GaAs) is one of the newest materials for microelectronics and optoelectronics. Its advantage over the commonly used silicon arises from a considerable resistance against radiation, broad temperature working range, high speed and relatively low electric power demand in the electronic devices.

The favourable properties of the GaAs crystals deteriorate easily if impurities already at trace level are present in the crystal lattice. Thus, sensitive and selective analytical methods are needed to control the purity of GaAs materials. Unfortunately only few analytical methods enable a direct analysis of GaAs samples, *e.g.* activation analysis [1—5], mass spectrometry [3, 6—10], graphite furnace atomic absorption spectrometry with solid sampling [11, 12]. The disadvantage of the above methods lies in high costs and lack of reference materials.

The other alternative is to analyze the GaAs samples by common analytical techniques after dissolving the samples and adjusting properly the sample solutions. Various methods have been used for the analysis of such sample solutions, *e.g.* stripping voltammetry [13—17], atomic absorption spectrometry (AAS) [18—34], flame atomic emission spectrometry (FAES) [35—38], atomic emission spectrography [39, 40], UV—VIS molecular absorption spectrometry [13, 41].

The matrix elements of the GaAs samples can significantly influence the analytical signal in most methods and therefore they should be removed by using some preconcentration technique, *e.g.* evaporation of Ga and/or As [42,

43], coprecipitation of the trace elements, separation by ion exchange or extraction [20, 44, 45].

Traces of sodium and potassium can significantly deteriorate the electric properties of GaAs semiconductive materials. Due to the high natural occurrence of these elements, they can easily contaminate the GaAs materials during processing. Relatively few papers have been published dealing with the determination of these elements in GaAs samples. Since the matrix elements have an adverse effect on the analytical signal when determining Na and K, combined methods are commonly used. The matrix elements can be extracted with tributyl phosphate [35] and Na and K can be determined in the remaining aqueous phase by atomic emission spectrography or flame atomic emission spectrometry. Traces of lithium were determined by FAES after the separation of the matrix elements by extraction with butyl acetate [36]. In gallium of high purity, sodium and potassium were determined without removing the matrix [37]. On the other hand, in the analysis of highly pure arsenic the matrix was removed by evaporation in chlorine as $AsCl_3$ and the residue was analyzed for Na and K by FAES [38].

This paper presents a simple procedure for the determination of Na and K in GaAs samples by graphite furnace atomic absorption spectrometry (GFAAS). FAES combined with the removal of the matrix elements by extracting with butyl acetate or tributyl phosphate was used to check the accuracy of the results.

Experimental

A double-beam atomic absorption spectrometer AAS 3 operating in the single-beam regime and using deuterium lamp background correction was used. The spectrometer was equipped with the graphite furnace atomizer EA-3 using pyrolytically coated graphite tubes (all Zeiss, Jena). The operating conditions and temperature programs are listed in Table 1. Peak area was measured as the analytical signal.

For the FAES measurements the two-channel flame photometer Flapho-4 (Zeiss, Jena) was used. The selection of the emission spectral lines for Na (λ = 589.0 nm) and K (λ = 766.5 nm) was performed using interference filters.

The used laboratory ware was cleaned by steaming with HNO_3 and water for 3 h in a steaming device [46, 47]. The operations with the GaAs samples and solutions were carried out in a box with laminar flow of filtered air.

Reagents used: 5—10 M hydrochloric acid, prepared by isothermal distillation in a teflon vessel; bromine (Laborchemie, Apolda, Germany), purified by distillation in a quartz apparatus; n-butyl acetate (BuAc) and tri(n-butyl) phosphate (TBuP) synthesized and purified [48]; NaCl and KCl (anal. grade purity) dried at 105 °C for 5 h and stored in a desiccator; doubly distilled deionized water (DDW) stored in a quartz or polypropylene flask.

Table 1

Operating conditions of the GFAAS instrument[a]

Parameter	Na	K
Wavelength/nm	589.6 or 589.0	769.6 or 766.5
Slit size/mm	0.20	0.20
Lamp current/mA	5	4
Drying I	95—20—5—280	95—20—5—280
Drying II	105—5—3—280	105—5—3—280
Pre-ashing	—	300—50—5—160
Ashing	500—100—3—160	500—100—3—160
Atomizing	1800—2000—2—*b*	2000—2000—2—*b*
Cleaning	2500—500—2—280	2500—500—2—280
Conditioning	2000—NP—5—160	2000—NP—5—160
Sample volume/mm^3	5—50	5—50

a) In the temperature programs: Final temperature/°C—Ramp/(°C s^{-1})—Hold/s—Argon gas flow/(cm^3 min^{-1}) inside the tube. *b*) Gas flow adjusted to 0—280 cm^3 min^{-1} depending on the concentration of the analyte. NP — no power heating.

The GaAs sample was powdered between two teflon sheets and etched in 10 M-HCl for 10 min. After washing with DDW and acetone the sample was dried and stored in a teflon vessel.

Procedure for the GFAAS method

The GaAs sample (20—100 mg) was weighted to a dry 4 cm^3 calibrated quartz test tube and 5—10 M-HCl (0.1 cm^3) was added. Bromine was added dropwise until the sample was completely dissolved. To avoid an intense reaction at the beginning of the dissolution procedure, the test tube was cooled in water. After the sample had been dissolved, about 0.5 cm^3 DDW was added, the solution was homogenized and the sample volume was adjusted to 1—3.5 cm^3 depending on the expected concentration of Na or K. The sample solution was analyzed using the standard addition technique.

Procedure for the FAES method

The GaAs sample (0.2—0.35 g) was weighted into a 20 cm^3 quartz test tube and 10 M-HCl (0.2—0.35 cm^3) was added. Bromine of the total volume 0.25—0.4·cm^3 was added dropwise. To accelerate the dissolution of the last portions of the sample the test tube can be slightly heated. After the dissolution had been accomplished, BuAc (2 cm^3) was added and the solution was intensively mixed for 3 min. The phases were allowed to separate, the organic phase was removed using a polyethylene syringe and fresh BuAc was added. The extraction was repeated, the aqueous phase was diluted to 1 cm^3 with

DDW and analyzed by FAES. The calibration was performed using the calibration curve method. Calibration curves were constructed for solutions with concentrations of Na and K from 0.08 to 1.0 μg cm^{-3}

Results and discussion

The determination of Na and K in solution containing Ga and As is handicapped by the disturbing effects of the matrix. The sensitivity of the analytical signal (peak area) in the GFAAS measurements depends significantly on the concentration of GaAs in the sample solution (Fig. 1). This sensitivity decrease is probably due to interferences of free Na and K atoms with gallium(III) oxide in the vapour phase during the atomization step like in the case of Zn determination [24]. For calibration the more laborious standard addition technique has therefore to be used.

The sensitivity of the measurement should be accommodated to the concentration of determined elements in the sample solution. The following ways have been used to match the signal sensitivity to the analyte concentration: *a*) choice of the most convenient absorption wavelength, *b*) sample dilution degree, *c*) adjustment of the argon gas flow in the graphite tube during the atomization step and *d*) adjustment of the sample volume injected into the graphite tube.

For both elements two wavelengths with different sensitivity have been used (Table 1), depending on the concentration of Na and K in the sample solution. The second way enabled to set the sample dilution degree from 0.1 g GaAs in 1 cm^3 to 0.02 g GaAs in 3.5 cm^3 sample solution. The argon gas flow in the graphite tube (way *c*) can be adjusted from 0 $cm^3\ min^{-1}$ (gas stop regime — the

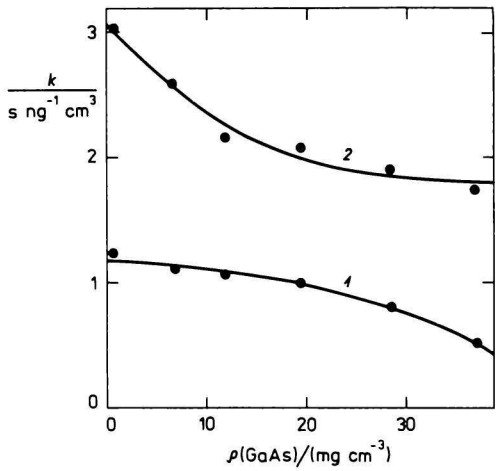

Fig. 1. Dependence of the signal sensitivity k on the concentration of GaAs in the sample solution for Na (*1*) and K (*2*).

Table 2

Analytical figures of merit

Method	Element	Sample amount mg	Concentration range[a] ϱ/(μg cm $^{-3}$)	$\frac{s_r}{\%}$[b]	Blank value ng	Detection limit (3s)[c] ppm
GFAAS	Na	20—100	0.03—10	15 (4.2)	15	0.011
	K	20—100	0.03—10	21 (3.1)	30	0.010
FAES	Na	200—350	0.1—10	18 (5.5)	40	0.03
	K	200—350	0.1—10	16 (6.7)	50	0.03

a) The upper concentration limit depends on the sample dilution degree; here, a maximum volume of 3.5 cm^3 and 2 cm^3 was considered for the GFAAS and FAES methods, respectively.

b) Calculated from the results of analyses of five samples separately weighed and dissolved. The values in parentheses were obtained from five repeated analyses of the same sample solution.

c) Valid for 0.1 g GaAs in 1 cm^3 sample solution (GFAAS) and for 0.2 g GaAs in 1 cm^3 sample solution (FAES), respectively, standard deviation.

highest sensitivity) to 280 cm^3 min^{-1} The sample volume injected into the graphite tube in the manual sampling mode could be 5 to 50 mm^3 Using one or more of these sensitivity matching possibilities, Na and K could be determined in the GaAs samples in the range from 0.03 to 10 ppm.

The temperature programs used are listed in Table 1. There is a conditioning step for both elements in these programs ensuring higher reproducibility. Omitting this step can cause a high scatter of the results. The plausible explanation for this observation is that at the cleaning step, due to the high temperature, sodium and potassium could be released from the body of the atomizer to the tube. The successive conditioning step removes this contamination from the tube.

In signal processing the peak area was measured instead of the more commonly used peak height measurements. The former method ensures linearity for a broader concentration range than the latter.

The blank values for Na and K depend significantly on the purity of reagents, vessels and on the quality of laboratory air. Reasonably low blanks can only be gained if freshly obtained DDW and hydrochloric acid prepared by isothermal distillation have been used. Since air contamination for Na and K has been severe, all the operations except for measurements on the AAS instrument are carried out in a clean box.

The analytical figures of merit for the GFAAS method are listed in Table 2. The reproducibility of the results is expressed as the relative standard deviation s_r. Analyzing repeatedly a given sample solution the reproducibility was better than 5 %, which is typical for GFAAS measurements. Much more unfavourable

results were obtained for analyses of different crystals of the same sample. Inhomogeneity in Na and K distribution in the GaAs crystals caused probably the higher scatter of the results.

To check the accuracy of the results in the GFAAS measurements a combined procedure using sample matrix extraction and determination of Na and K by FAES was used. As extractants TBuP and BuAc were checked. The former solvent needs longer extraction times than the latter, moreover the separation of the phases is faster for the latter. BuAc was therefore preferred in further experiments.

The extraction time influences the reproducibility of the results (Table 3). After 3 min extraction the reproducibility changes little so this extraction time was chosen as optimum.

Preliminary observations have shown that like in the GFAAS measurements the purity of reagents and vessels exerts a predominant influence on the blanks and the reproducibility of the results. Due to the preconcentration step there was an enhanced danger of contamination.

Table 3

Influence of the time of mixing in the extractions with BuAc on the results

Time of mixing	w(found)/ppm	
min	Na	K
1	0.32 ± 0.11	0.23 ± 0.13
2	0.30 ± 0.08	0.24 ± 0.10
3	0.28 ± 0.06	0.22 ± 0.05
4	0.29 ± 0.06	0.22 ± 0.05
5	0.28 ± 0.06	0.23 ± 0.05

Table 4

Recovery test for the FAES method (obtained from five analyses)

ϱ(given)/(μg cm $^{-3}$)	ϱ(found)/(μg cm^{-3})	
	Na	K
0.08	0.075 ± 0.015	0.085 ± 0.017
0.16	0.163 ± 0.025	0.164 ± 0.017
0.25	0.248 ± 0.025	0.253 ± 0.025
0.35	0.353 ± 0.029	0.352 ± 0.028
1.0	1.10 ± 0.18	1.01 ± 0.13

Table 5

Comparison of the results for GFAAS and FAES (calculated from five measurements)

ϱ(Na)/(μg cm $^{-3}$)		ϱ(K)/(μg cm $^{-3}$)	
GFAAS	FAES	GFAAS	FAES
2.6 ± 0.3	2.5 ± 0.5	6.1 ± 2.0	6.2 ± 1.5
7.6 ± 0.6	7.3 ± 1.2	2.2 ± 0.2	1.9 ± 0.5
3.5 ± 0.5	3.3 ± 0.5	3.4 ± 0.5	3.6 ± 1.0
5.8 ± 0.7	5.2 ± 0.8	2.6 ± 0.5	2.7 ± 0.6

The extraction recovery was checked as follows: the 10 M-HCl (1 cm^3) was purified by extraction with BuAc (2 cm^3). Known amounts of Na and K were then added to the aqueous phase and the analysis was accomplished as described in Experimental. The results are listed in Table 4. In the tested concentration range recoveries between 93 and 106 % were achieved.

The elaborated methods were used for the analysis of various GaAs samples. Some representative results are collected in Table 5. The reproducibility of the GFAAS method is better than that for the FAES method, moreover lower detection limits can be obtained. The former method is simpler and much faster. A complete analysis involving sample dissolution, repeated measurement and standardization for both elements takes about 30 min per sample. The FAES method is more complex and time-consuming; a complete analysis of one sample takes about 2 h. Its use is adequate for checking the accuracy of other methods or when the GFAAS instrument is not available.

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