

Multicomponental Fluorimetric Determination of Aluminium, Gallium and Indium

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Abstract For the fast characteristics of mixtures of Aluminium, Gallium and Indium the fluorimetric evaluation in the form of complexes with 8-Hydroxyquinoline-5-sulphonic acid is described at selected pH. The highly collinear correlated fluorescent spectra and their first derivation were evaluated under various experimental conditions with the Multiple Linear Regression (MLR), Partial Least Squares (PLS) methods and Kalman filtering. When comparing the results, the PLS gives the least relative prediction errors under optimal conditions, 5.6–15.9% for the concentration range of Al 0.025–0.2 $\mu\text{g cm}^{-3}$, Ga 0.1–0.8 $\mu\text{g cm}^{-3}$ and In 0.1–0.8 $\mu\text{g cm}^{-3}$ in the mixture.

Keywords 8-hydroxyquinoline-5-sulphonic acid · Multivariate evaluation · Aluminium · Gallium · Indium complexes · Fluorescence

Introduction

The simultaneous fluorimetric determination of Aluminium, Gallium and Indium in their complexes with 8-hydroxyquinoline

after their extraction into chloroform has been reported recently [1]. The normal and derivative excitation and fluorescence spectra were evaluated by using the Multiple Linear Regression (MLR) and Partial Least Squares (PLS) methods under selected conditions. The MLR method have been also applied to the three dimensional diagrams of fluorescence intensity dependence on both excitation and emission wavelength. Some general results and experiences follow from the studies [1, 2] for the multivariate system with high extent of collinearity when excitation and fluorescence spectra are simultaneously evaluated. MLR was not found to be a suitable method for evaluation of these ternary mixtures due to the highly overlapped and virtually identical excitation and emission spectra profile. Evaluation of three dimensional diagram did not bring significantly better results and first derivative spectra evaluation was even much poorer because of increased spectral noise. The PLS method can minimize collinearity problems and enables correct resolution of the mixtures.

In this paper, the results of Multiple Linear Regression (MLR) [3], the regression of latent variables of measured quantities against latent variables of concentration values of analytes with full projection to latent structures—Partial Least Squares (PLS) [3–9] and Kalman filtering [10–15] are compared for the fluorescent spectra of mixtures of Aluminium, Gallium and Indium complexes with 8-hydroxyquinoline-5-sulphonic acid in aqueous solutions under various experimental conditions. The prediction error of the enquired analyte concentrations depends on the character and the overlapping of the particular spectra of the components, the number and selection of wavelengths, the number of the calibration solutions and the design of used statistical plan of the calibration set. The Kalman filtering is usually suitable for the interpretation of very similar spectra of the particular components as well as the derivation of spectra enabling the better distinguishing of

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signals of the particular components [16]. However no advantage was observed in our case.

Experimental

Chemicals

Standards used, Analytica s.r.o., Prague

Aluminium chloride $1.000 \pm 0.002 \text{ g l}^{-1}$ containing 5% HCl

Gallium chloride $1.000 \pm 0.002 \text{ g l}^{-1}$ containing 10% HCl
Indium chloride $1.000 \pm 0.002 \text{ g l}^{-1}$ containing 10% HCl

8-Hydroxyquinoline-5-sulphonic acid hydrate (QSA), Sigma-Aldrich was used without purification

Other chemicals used were of analytical grade purity.

Surface water was sampled from The Tatra Mountains lake (Slovakia), filtered on a dense filter paper and stored in dark bottles. Macrocomponents determined by ICP-AES were Ca (4,459 ppm), Mg (0,2244 ppm) and Na (1,277 ppm). The concentrations of natural Al, Ga and In, if present, were below the detection limit. Suitable amounts of Aluminium, Gallium and Indium were added according to statistical plan (Table 1) and the solutions were equilibrated in darkness and analyzed after 24 h.

Instruments

Spectrofluorimeter Aminco Bowman, Series 2 with 1 cm quartz cells, 4 nm exit slits, photomultiplier under 450–850 V. Sample cell was tempered to 20 °C.

The calculation of the first derivative was done by using the instrument software using Golay-Savitzky 11-point convolution.

The pH meter of WTW level 3 with a glass electrode standardized with pH 4.0 and pH 7.0 buffers was used.

Preparation of working solutions

The individual working solutions were pipetted in the following order: an acidic solution of the test metal ion or a mixture of test ions and the reagent solution. Selected pH was adjusted with diluted hydrochloric acid or sodium hydroxide. For the measurement pH 4 was adjusted and 730 V photomultiplier voltages were used.

Evaluation of data

Evaluation by Partial Least Squares (PLS) method

The program PLS-G [17] written on the basis of algorithms [18] in Fortran was used for the evaluation.

Table 1 Calibration set for CFD, FFD+CP(*), test set and model set

Sample	Coded levels			Concentrations ($\mu\text{g cm}^{-3}$)		
	Al	Ga	In	Al	Ga	In
Calibration set						
1*	+	+	+	0.2	0.8	0.8
2	+	+	0	0.2	0.8	0.4
3*	+	+	–	0.2	0.8	0.1
4	+	0	+	0.2	0.4	0.8
5	+	0	0	0.2	0.4	0.4
6	+	0	–	0.2	0.4	0.1
7*	+	–	+	0.2	0.1	0.8
8	+	–	0	0.2	0.1	0.4
9*	+	–	–	0.2	0.1	0.1
10	0	+	+	0.1	0.8	0.8
11	0	+	0	0.1	0.8	0.4
12	0	+	–	0.1	0.8	0.1
13	0	0	+	0.1	0.4	0.8
14*	0	0	0	0.1	0.4	0.4
15	0	0	–	0.1	0.4	0.1
16	0	–	+	0.1	0.1	0.8
17	0	–	0	0.1	0.1	0.4
18	0	–	–	0.1	0.1	0.1
19*	–	+	+	0.025	0.8	0.8
20	–	+	0	0.025	0.8	0.4
21*	–	+	–	0.025	0.8	0.1
22	–	0	+	0.025	0.4	0.8
23	–	0	0	0.025	0.4	0.4
24	–	0	–	0.025	0.4	0.1
25*	–	–	+	0.025	0.1	0.8
26	–	–	0	0.025	0.1	0.4
27*	–	–	–	0.025	0.1	0.1
Test set						
T1	+0.5	–0.5	–0.5	0.15	0.25	0.25
T2	–0.5	+0.5	+0.5	0.0625	0.6	0.6
T3	–0.5	+0.5	–0.5	0.0625	0.6	0.25
T4	–0.5	–0.5	+0.5	0.0625	0.25	0.6
Model set						
M1	+0.6	+0.6	–	0.16	0.64	0.1
M2	–0.266	0	–0.933	0.08	0.4	0.12

The calculations by the PLS method are carried out in two basic steps. In the first step (calibration) a search is made for a relationship between the fluorescence data matrix with elements F_{np} where n is the number of calibration mixtures and p is the number of wavelengths, and the concentration matrix with elements c_{nm} where m is the number of determined components. This is realized by the assessment of the number of main (abstract) components and contemporaneous regression and rotation of transformed matrixes F_{np} and c_{nm} . In the second step (prediction) the concentration values of the individual components are determined in the sample. These concentrations are calculated from the measured sample fluorescence values using the relationship found in the calibration

Fig. 1 Comparison of excitation and emission spectra of particular complexes with $0.3 \mu\text{g}\cdot\text{cm}^{-3}$ of each element in the presence of $7.4 \times 10^{-5} \text{ mol dm}^{-3}$ QSA at 715 V and pH 4 for Al, pH 3 for Ga and pH 8 for Al

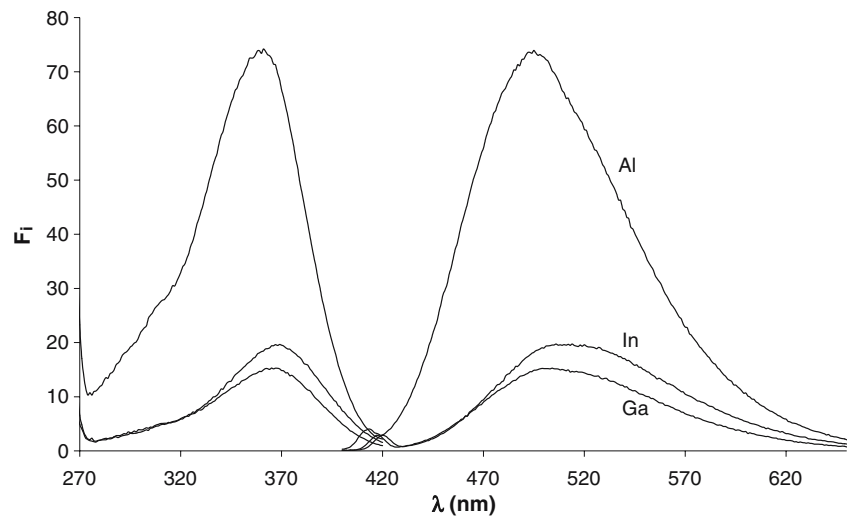


Fig. 2 Fluorescence intensity dependence on pH for particular complex with $0.3 \mu\text{g cm}^{-3}$ of each element in the presence of $7.4 \times 10^{-5} \text{ mol dm}^{-3}$ QSA at 715 V

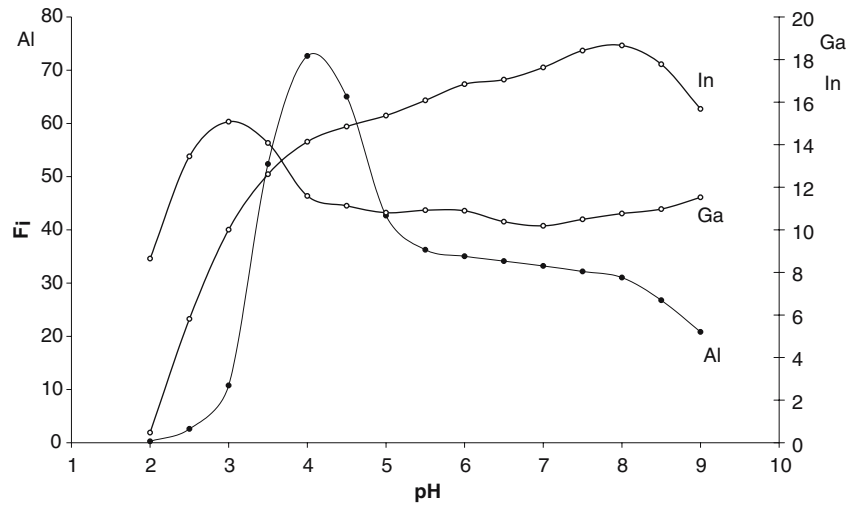


Fig. 3 Comparison of emission spectra of particular complexes (pure components) for $0.2 \mu\text{g cm}^{-3}$ Al, $0.8 \mu\text{g cm}^{-3}$ Ga and In (Kalman filtering calibration set) in the presence of $1.8 \times 10^{-4} \text{ mol dm}^{-3}$ QSA at 730 V and pH 4

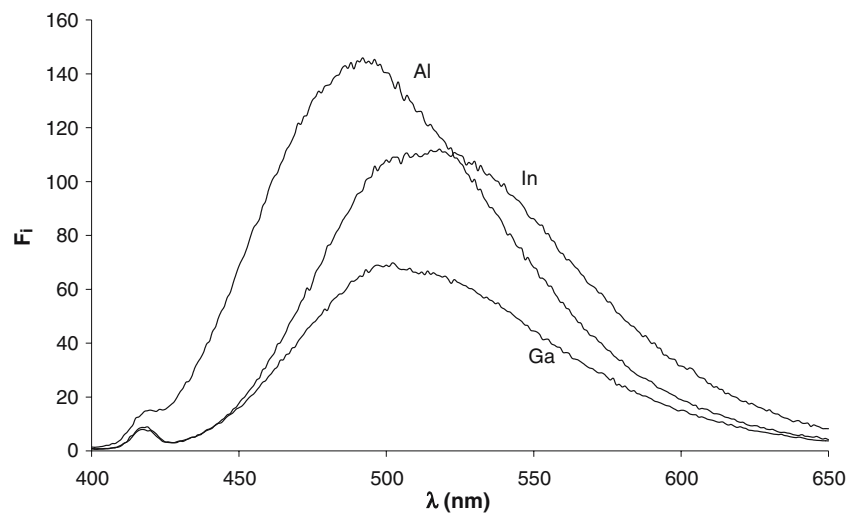


Table 2 Comparison of prediction errors for various calibration sets and wavelength numbers

No. of solutions	No. of λ	SRPE (%)						CRPE (%)			MRPE (%)
		T1	T2	T3	T4	M1	M2	Al	Ga	In	
27	24	13.3	4.3	34.5	9.0	8.5	12.8	11.0	19.7	9.9	13.7
27	16	7.5	6.7	7.8	5.2	2.3	3.9	12.8	6.0	4.9	5.6
9	24	20.3	26.7	14.2	6.3	16.3	11.6	12.7	23.1	8.2	15.9
9	16	2.9	8.4	5.8	22.5	4.4	6.0	12.6	12.9	7.7	8.3

phase. The number of significant main components in the PLS algorithm was determined by cross-validation [19]. The algorithm and mathematical basis of the PLS method are described in detail in refs [4, 18, 20, 21].

The strictly linear calibration dependences for fluorescence were acquired for the evaluation. The identical conditions for the calibration and test solutions are required for the evaluation.

The basic criterion for correctness of the results obtained by PLS calculation is agreement of the actual (given) concentrations of the individual components with the calculated (predicted) values expressed by the following relations:

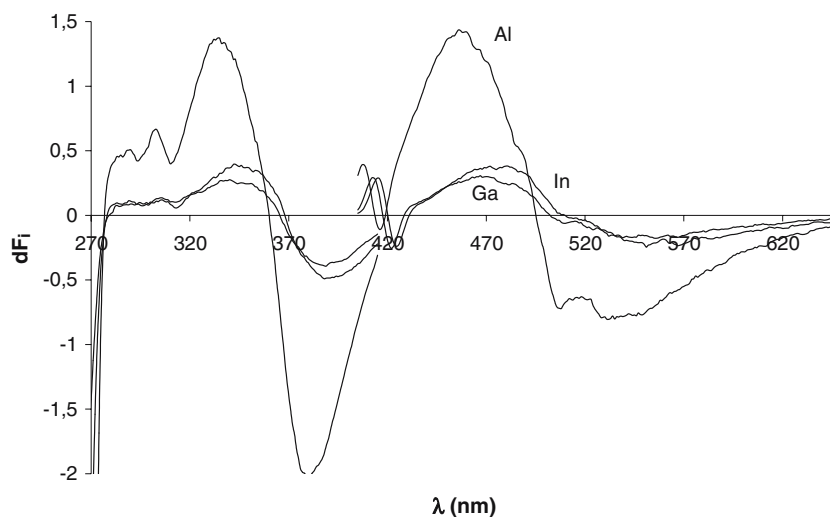
Component Relative Prediction Error (CRPE)

$$CRPE_j = \sqrt{\frac{\sum_{i=1}^T (c_{ij} - \hat{c}_{ij})^2}{\sum_{i=1}^T c_{ij}^2}} \cdot 100 \quad [\%]$$

Sample Relative Prediction Error (SRPE)

$$SRPE_i = \sqrt{\frac{\sum_{j=1}^M (c_{ij} - \hat{c}_{ij})^2}{\sum_{j=1}^M c_{ij}^2}} \cdot 100 \quad [\%]$$

Fig. 4 Comparison of first derivative excitation and emission spectra of particular complexes ($0.3 \mu\text{g cm}^{-3}$ of each element) in the presence of $7.4 \times 10^{-5} \text{ mol dm}^{-3}$ QSA at 715 V and pH 4 for Al, pH 3 for Ga and pH 8 for Al



Multicomponent Relative Prediction Error (for all components and samples) (MRPE)

$$MRPE = \left[\sum_{i=1}^T \sqrt{\frac{\sum_{j=1}^M (c_{ij} - \hat{c}_{ij})^2}{\sum_{j=1}^M c_{ij}^2}} \right] \cdot T^{-1} \cdot 100 \quad [\%]$$

where T is the number of test solutions (samples), M is the number of components and c_{ij} and \hat{c}_{ij} are the actual and calculated concentration values of the particular components.

The error of the predicted concentrations of the components is influenced by the number of wavelengths and calibration solutions and design of the statistical plan of the calibration set [16, 22–24]. The found CRPE and MRPE enable to evaluate the predicted errors of the calculated unknown component concentrations in the analyzed samples when the conditions for calibration and testing solutions are identical.

Evaluation by Kalman filtering

For the evaluation of data the program KF-G [16] written in Turbo Pascal, on the basis of algorithms [10, 14], was used. This algorithm is completely different from PLS algorithm

Table 3 Interpretation of calibration plots for QSA complexes with Al, Ga and In

	AlQSA	GaQSA	InQSA
E(V)	620	750	830
Concentration range ($\mu\text{g cm}^{-3}$)		0.004–1	
Normal fluorescent spectra			
$\lambda_{\text{max(em)}} \text{ (nm)}$	495	504	506
Regression equation	51.98x+0.9186	78.46x+1.1235	185.06x+10.75
Correlation coefficient	0.9991	0.9992	0.9995
Derivative fluorescent spectra (peak-to-peak)			
$\lambda_{\text{max(em)}/\lambda_{\text{min(em)}} \text{ (nm)}$	460/542	472/552	478/560
Regression equation	1.5933x+0.0262	2.4467x+0.017	5.7551x+0.3465
Correlation coefficient	0.9990	0.9996	0.9990

(where the criterion of agreement among calculated and evaluated data is the least squares sum) and it's based on the theory of probability. The parameters of the model for the concentrations of the components are determined by the Bays estimate on the basis of condition probability for which the estimated values for the *j*th wavelength are predicted from the values predicted for the 1st, ..., (*j*-1)th wavelength. The criterion of the agreement among the model and the data is the mean quadratic error of estimated parameters [25]:

$$S^2 = (Y_d - Y_j)^2$$

where *Y_d* is the given and *Y_j* the predicted value of the function *Y* with *j*=1... *p* for *p* wavelengths. Thus the error of the determined parameters is minimized step by step for each wavelength. The model for the Kalman filtering consists of the two parts, the model of system dynamics which is the change of the signal with the time and the model of measurement which is the strict additivity of signals of the particular components. When no dynamics of the system is observed (concentrations of components are constant during measurement) the model of measurement is only used for the calculation of *Y*. In contrast to PLS no suitable calibration set and wavelengths need to be chosen, but spectra of the pure components and the variance of the noise must be known.

Evaluation by the Multiple Linear Regression (MLR) method

A new version of MLR-G program in Microsoft Excel® environment was used in this paper for evaluation by this simple and well known method of multivariant calibration. Two steps, the calibration and prediction are used again.

During the calibration the mathematical relation between the data matrix of **F_{ij}** (*i*=1...*n* and *j*=1...*p*, where *n* is the number of solutions in the calibration set and *p* is the number of wavelengths) and the concentration matrix **C_{ik}** (*i*=1...*n* and *k*=1...*m*, where *n* is the number of solutions and *m* the number of components) is realized (without assessment of the number of main components and rotation of matrixes) by the finding of projection matrix **P**.

$$\mathbf{C} = \mathbf{F} \times \mathbf{P},$$

in order to sum of the least squares to be minimal:

$$U = \sum_{i=1}^n \sum_{k=1}^m (c_{ik} - \hat{c}_{ik})^2$$

where *c_{ik}* and \hat{c}_{ik} are the given and calculated concentration values of the particular components.

During the prediction, the concentrations of particular components are calculated from the measured sample fluorescence values using the relationship (matrix **P**) found in the calibration phase. This simple procedure has some shortening. During the matrix inversion in the presence of a large number of wavelengths some of the columns of the **Y** matrix are almost linearly dependent. Moreover the accumulation of errors can appear. For this reasons, the MLR is convenient for solution of simpler problems.

Results and discussion

The complexes of 8-Hydroxyquinoline-5-sulphonic acid with Al, Ga, and In produce an outstanding fluorescence for

Table 4 Prediction errors for the first derivative spectra in the middle wavelength region for various calibration sets and wavelength numbers

No. of solutions	No. of λ	SRPE (%)						CRPE (%)			MRPE (%)
		T1	T2	T3	T4	M1	M2	Al	Ga	In	
27	24	17.6	1.1	15.6	24.5	29.8	10.3	8.6	21.8	12.9	16.5
27	16	40.4	11.0	13.8	15.2	34.0	6.1	8.7	24.0	15.4	20.1
9	24	36.4	15.7	37.6	27.7	39.8	24.6	10.4	36.4	16.4	30.3
9	16	35.9	15.7	37.8	27.8	40.2	25.3	10.4	36.8	15.9	30.5

Table 5 Prediction errors for the first derivative spectra in the shorter and longer wavelength region for various calibration sets and wavelength numbers

No. of solutions	No. of λ	SRPE (%)						CRPE (%)			MRPE (%)
		T1	T2	T3	T4	M1	M2	Al	Ga	In	
418–510 nm											
27	24	33.9	8.3	16.8	18.2	17.4	17.6	16.8	20.2	9.1	18.7
27	16	11.4	2.3	21.4	5.8	8.8	36.2	16.1	16.4	11.2	14.3
9	24	35.0	14.4	37.0	30.0	41.6	24.1	8.4	36.8	17.0	30.3
9	16	32.6	13.7	37.5	30.8	43.1	25.8	8.4	37.0	18.6	30.6
510–602 nm											
27	24	55.5	3.3	9.6	25.5	31.3	24.3	10.5	28.9	12.5	24.9
27	16	39.2	17.8	37.1	25.5	37.9	20.8	20.7	36.0	15.0	29.7
9	24	40.8	17.6	36.9	26.1	36.3	20.3	10.9	35.8	14.4	29.7
9	16	42.0	18.5	37.2	23.9	36.4	20.3	14.3	35.5	15.5	29.7

wavelengths over 430–600 nm with λ_{max} at 495 nm for Al, λ_{max} at 504 nm for Ga and λ_{max} at 519 nm for In, while a very little difference is observed for excitation spectra with λ_{max} about 365 nm (Fig. 1). Considerable difference is observed in pH dependence of fluorescence maximum. The highest fluorescence was found at pH 4 for Al, pH 3 for Ga and pH 8 for In (Fig. 2).

Optimal reagent concentration in solution without self-quenching was found to be 3.5×10^{-5} – 7.4×10^{-5} M. The formation of fluorescent complexes is instantaneous and the fluorescence remains stable for at least 12 h.

Strictly linear calibration plots appear for concentrations less than 1 mg l^{-1} at Photomultiplier Feeding 620–830 V. For the multicomponent determination the 730 V photomultiplier voltage was used.

A strong overlapping of fluorescence spectra of complexes for 480–530 nm is observed (Fig. 3). For the calculation the wavelength region 420–600 nm was used. Excitation spectra were not used for the interpretation due to their stronger overlapping. Because the Aluminium complex behaves as major component with more than four

times higher fluorescence against other components, its concentration has been quartered.

The multicomponent analysis of mixture of Al, Ga and In complexes with QSA has been realized by three methods of multivariate calibration: PLS, Kalman filtering and MLR.

Results for PLS

Two calibration sets were examined, the Complete Factorial Design (CFD) and the Fractional Factorial Design (FFD) for 3, respective 2 concentration levels and in the presence of Central point (CP).

$$n_{\text{CFD}} = L^m \text{ (27 solutions)}$$

$$n_{\text{FFD}} = L^m + CP \text{ (9 solutions)}$$

where n is the number of calibration solutions, m is the number of components and L is the number of concentration levels.

The used statistical designs with 24 or 16 wavelengths were examined against relative prediction errors (CRPE%, MRPE%) using six testing solutions. Four of them were

Fig. 5 Comparison of first derivative emission spectra of particular complexes (pure components) for $0.2 \mu\text{g cm}^{-3}$ Al, $0.8 \mu\text{g cm}^{-3}$ Ga and In (Kalman filtering calibration set) in the presence of $1.8 \times 10^{-4} \text{ mol dm}^{-3}$ QSA at 730 V and pH 4

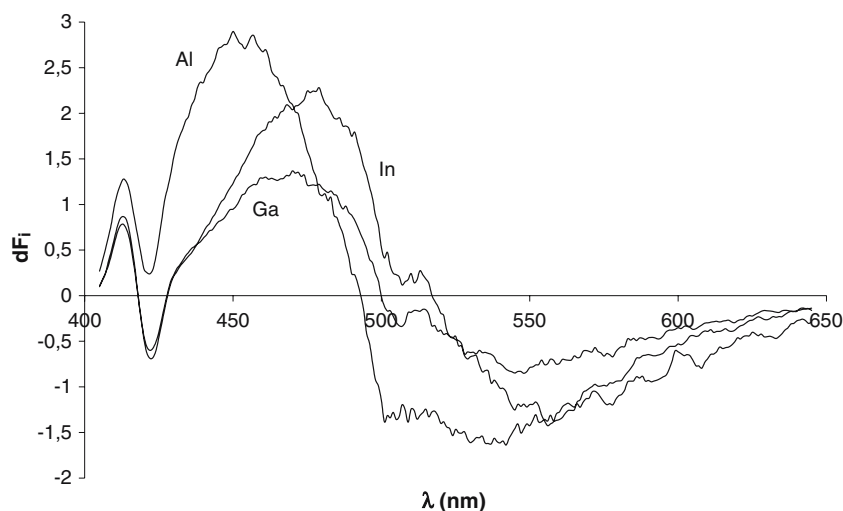


Table 6 Calibration set (KF, MLR) and test set (KF, MLR, PLS)

Sample	Coded levels			Concentrations ($\mu\text{g cm}^{-3}$)		
	Al	Ga	In	Al	Ga	In
Calibration set						
1	+	-	-	0.2	0	0
2	-	+	-	0	0.8	0
3	-	-	+	0	0	0.8
Test set						
S1	0	0	0	0.1	0.4	0.4
S2	-0.5	+0.5	+0.5	0.0625	0.6	0.6
S3	-0.5	+0.5	-0.5	0.0625	0.6	0.25

selected to the 1/4 and 3/4 levels of extent of concentrations of the calibration set (Test set) and the rest of them accidentally (Model set). The coded structure with two limiting and the middle concentration levels, the coded structure of the Test set and the Model set with the actual concentrations are shown in Table 1.

Four cases for different plans and number of wavelengths were evaluated and compared:

27 calibration solutions (CFD) and 24 wavelengths (462–554 nm with 4 nm step)

Table 7 Comparison of prediction errors for PLS, KF and MLR for various calibration sets and wavelength numbers

Number of calibration solutions	Number of λ	Sample	CRPE (%)			MRPE (%)
			Al	Ga	In	
27	24	S1	-7.8	-13.0	10.7	10.5
		S2	1.1	-0.1	-6.1	2.4
		S3	30.3	-35.2	30.4	32.0
27	16	S1	3.7	-23.2	7.7	11.5
		S2	11.0	-8.6	-3.8	7.8
		S3	22.8	-8.1	-0.9	10.6
9	24	S1	-0.4	10.1	-3.4	4.6
		S2	21.3	-37.0	7.4	21.9
		S3	-0.4	-13.7	17.1	10.4
9	16	S1	-2.2	-21.5	10.9	11.5
		S2	17.3	-11.1	-3.8	10.7
		S3	-3.4	-6.3	0.9	3.5
Kalman filter						
3	24	S1	8.9	-58.7	-2.8	23.5
		S2	-13.5	-38.7	11.6	21.2
		S3	-22.7	-4.4	23.3	16.8
3	48	S1	-3.2	6.1	-24.4	11.2
		S2	-1.0	-25.9	-10.7	12.5
		S3	-2.3	-0.4	-25.7	10.8
MLR						
3	24	S1	4.0	-46.8	-1.1	17.3
		S2	12.1	-58.8	3.9	25.0
		S3	2.1	-19.6	-6.0	9.2

Table 8 Comparison of mean relative prediction errors for PLS, KF and MLR for various calibration sets and wavelength numbers

Number of calibration solutions	Number of λ	MCRPE (%)			MMRPE (%)
		Al	Ga	In	
PLS					
27	24	13.1	16.1	15.7	15.0
27	16	12.5	13.6	4.1	10.0
9	24	7.3	20.3	9.3	12.3
9	16	7.6	13.0	5.2	8.6
PLS—surface water					
9	16	12.1	16.8	6.4	11.8
Kalman filter					
3	24	15.0	33.9	12.5	20.5
3	48	2.2	10.8	21.6	11.5
MLR					
3	24	6.1	41.7	3.7	17.2

27 calibration solutions (CFD) and 16 wavelengths (466, 474, 482, 490, 494, 498, 502, 506, 510, 514, 518, 522, 526, 534, 542, 550 nm)

9 calibration solutions (FFD+CP) and 24 wavelengths (462–554 nm with 4 nm step)

9 calibration solutions (FFD+CP) and 9 wavelengths (466, 474, 482, 490, 494, 498, 502, 506, 510, 514, 518, 522, 526, 534, 542, 550 nm).

The prediction errors SRPE, CRPE and MRPE in % for the previous experimental arrangements are in Table 2.

As follows from the Table 2 the calibration set CFD with 27 calibration solutions and 16 wavelengths gives the lowest prediction error.

The errors for particular components CRPE are the highest for Gallium because of its intermediate wavelength position of λ_{max} and its lowest signal against Al and In. Therefore the application of various scaling factors [23] (increase of statistical weight of particular component) for Ga as minority component was tested but no improvement for Gallium resulted. For this reason the scaling factor 1.0 was always used for all components.

The first derivative of fluorescence spectra of Al, Ga, and In complexes (Fig. 4) was also proved for its influence on the prediction errors using the same reaction conditions, statistic plans, the same calibration sets, test set, model set and wavelengths as above.

Like before, strictly linear calibration plots appear again under the same conditions for the Al, Ga and In complexes with 8-hydroxyquinoline-5-sulphonic acid using the peak-to-peak method for evaluation (Table 3).

Unfortunately no improvement for SRPE, CRPE and MRPE was observed. The values of errors are higher than those for normal fluorescence spectra because the first derivative spectra are more linearly dependent in the wavelength interval 462–554 nm (Table 4).

Moreover no improvement was found when the first derivative spectra were evaluated for a shorter wavelength interval between 418 and 510 nm where the spectra of Al, Ga and In complexes with the 8-Hydroxyquinoline-5-sulphonic acid show a positive derivative maximum. Evaluation of negative maximum of the 1st derivative spectra provides even worse results (Table 5).

This is connected with the rather high noise level of the first derivation of spectra (Fig. 5).

Comparison of the PLS with the Kalman filtering and MLR

The Kalman filtering was used for the fluorescence spectra using 24 wavelengths in the interval 462–554 nm with 4 nm steps and for 48 wavelengths in the interval 456–597 nm with the 3 nm steps. For the MLR the 24 wavelengths in the interval 462–554 nm with 4 nm steps were used.

The calibration set for Kalman filtering and MLR consists of the particular components spectra. The same test set of three samples was prepared for all methods and compared in Table 7. The coded structure of the calibration and test sets with the actual concentrations is collected in Table 6.

The prediction errors for all used multivariate methods with various types of calibration sets and the number of wavelengths are presented in Table 7.

Higher values for CRPE and MRPE for the KF and MLR come from the considerably overlapped spectra. Similarly worse results are again observed for the Gallium with the Kalman filtering and as was predicted with MLR. Lower prediction errors were obtained for the Kalman filter, which generally needs more wavelengths, when 48 wavelengths were used for the interpretation. In this case the errors correspond with those from the PLS.

Comparison of mean relative prediction errors (MCRPE, MMRPE) of particular methods calculated from all three samples is shown in Table 8.

Analysis of surface water

The same FFD+CP calibration set of PLS with 16 wavelengths have been applied for analysis in real samples of surface water with the same procedure and calibration of determination. Obtained prediction errors are summarized and compared to the previous results in the Table 8.

Conclusion

As apparent from the total mean CRPE and MRPE the multicomponent fluorimetric determination of Al, Ga and In with 8-Hydroxyquinoline-5-sulphonic acid gives satisfac-

tory results under selected conditions (pH 4, 1.8×10^{-4} mol dm^{-3} QSA, 730 V, less than $0.2 \mu\text{g cm}^{-3}$ of Al and $0.8 \mu\text{g cm}^{-3}$ of Ga and In), the statistic plan of calibration solutions and the number of wavelengths. The most suitable method is the PLS with the errors of 5.6–15.9% or 8.6–15.0% respectively, which represents a significantly better result than that for chloroform-extraction 8-hydroxyquinoline method [1]. The highest prediction errors, such as 6.0–23.1% or 13.6–20.3% for PLS, 10.8–33.9% for KF and 41.7% for MLR, was always found for Gallium because of considerably overlapped spectrum of Al and In.

The Kalman filtering falls short of expectations when used for the evaluation of fluorescent spectra in this system. Similarly the use of MLR is unsuitable for the evaluation of fluorescence spectra with a high extent of collinearity.

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