

SPECTRO REPORT

APPLIKATION REPORT 80

SPECTROFLAME ICP

THE ANALYSIS OF SODIUM CHLORIDE

SPECTRO Analytical Instruments GmbH, Kleve



INTRODUCTION

Sodium chloride is a product used in different industrial applications: in the field of food and fodder, in the medical field, and for the electrolysis to produce sodium hydroxide and chlorine gas (e.g. with the diaphragm process). The biggest natural resource of sodium chloride are the oceans (approx. 3% NaCl) and rock salt deposits.

After cleaning sodium chloride is used as a product for sodium hydroxide and chlorine gas production:



Due to the increase of boiling point and decrease of the freezing point of water through addition of sodium chloride, brines are also used as coolants.

Further applications are in the medical field. Here sodium chloride is indispensable as a solution for dialysis. This application requires a very high degree of purity. Especially limit values below 0.1 mg/kg for aluminum and some other heavy metals have to be controlled. The ESPA (European Salt Producing Association) has a standard for the

analysis of NaCl in preparation which describes the determination of some acid-soluble elements in NaCl using the optical emission spectrometry with an inductively coupled plasma.

Requirements for the analysis of NaCl

In the above applications the purity of NaCl has to be checked. Typical contaminations are in the concentration range between 0.02 and 30 mg/kg. Taking the detection limits of the ICP-OES into account (see Application Report 66), it is obvious that the necessary detection limits cannot be obtained in the usual 1 : 100 dilution, which are usual for other matrices. This is why the analysis has to be carried out in a base solution which is concentrated as much as possible.

For this purpose some conditions have to be met when feeding samples: High matrix concentrations (>2% weight) in the aerosol affect the efficiency of the nebulizer by a change of viscosity and may result in a crystallization process in the nebulizer and in the injector tube of the torch. The following instrument parameters are proved as advantageous for salt concentrations up to 20%:

ICP Power:	1300W
Coolant gas:	13 L/min Argon
Auxiliary gas:	1,5 L/min Argon
Nebulizer gas:	0,9 L/min Argon
Additional gas:	0,5 L/min Argon
Torch:	dismountable or fixed with Injector tube 2,5mm ID (for side-on view) dismountable or fixed with Injector tube 3,0mm ID (for end-on view) for both cases with additional gas adapter
Nebulizer:	Cross-flow, model SPECTRO
Argon humidifier:	to avoid crystallizations

SAMPLE PREPARATION

Crystalline sodium chloride (Merck, ‚suprapur‘) is dissolved in a concentration of 200 g/l. Before filling up to the required volume, a pH-value < 2 has to be adjusted using high-purity nitric acid. This requires 20 ml concentrated nitric acid per liter.

To analyze the elements bromine and iodine, it is not recommended to make a solution acid, because both elements change over in an acid medium to a gaseous state, escaping slowly the sample. A stabilization of the sample to analyze bromine and iodine is possible with a pH-value of 10.

Both, samples and standard solutions have to be produced in the same way, the matrix concentrations have to be identical. A ‚suprapur‘ sodium chloride is used as matrix solution, and then the respective agent is added to produce further calibration standards. A 3 or 5 point calibration is to be carried out for calibration. After standardization the medium standard is used to verify the calibration, because standardizations are performed only with the matrix solution and the high standard when analysing with ICP-OES. Concentrations below the detection limits are often analyzed, this is why the calibration curve in the range of the detection limit must be verified regularly. The control sample ‚blank‘ is intended for that purpose - in this case the matrix blank solution. The analysis result for the corresponding analysis agent of this solution must be ‚< detection limit‘ to confirm the correctness of the analysis close to the detection limit.

The following window (figure 1) shows an analysis sequence in the ‚command list editor‘ of the SPECTROFLAME Smartanalyzer software. The analysis sequence can be edited as described below by the operator. The analysis are automatically carried out with the sample feeder AS300 (SPECTRO).



Comments for the command list in figure 1:

- Call-up of the method (1st line)
- Calibration with the defined standards (2nd - 6th line)
- Carrying out the regression (a correlation coefficient defined by the operator is automatically checked and is used as a criterion for possible abort) (7th line)
- Analysis of a control sample ‚control‘ (8th line)
- Standardization with the matrix blank solution and the high standard (here: standard No 4) (9th and 10th line)
- Analysis of the calibration control standard ‚CV‘5 (here: standard No 2) (11th line)
- Analysis of the control sample ‚control‘ (standard No 3) (12th line)
- Analysis of the matrix blank solution ‚CB‘ (13th line)
- Analysis of the unknown samples ‚unknown‘ (14th - 18th line)

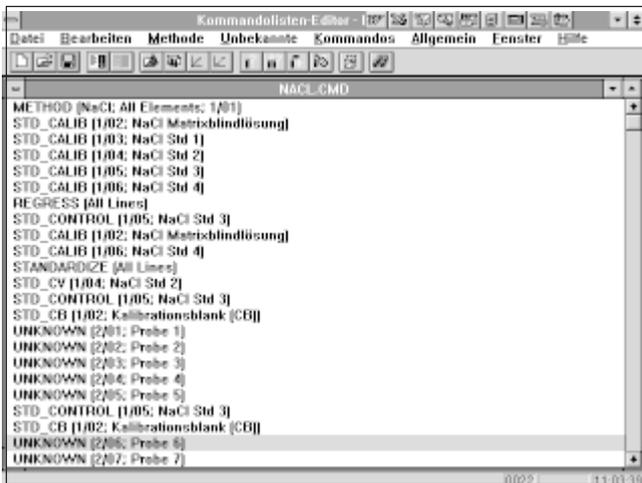


Figure 1: Analysis sequence in the command list editor of the Spectroflame Smartanalyzer software

Then the control sample measurement and the check of the matrix blank value are repeated and further samples are analyzed.

In the menu item ‚sample logic‘ of the program development of the Spectroflame Smartanalyzer software (figure 2) the operator may define a number of criteria: standard for verification of the calibration, calibration blank, control samples. Additionally the correlation coefficient, which is expected from the regression calculation, is entered into the window. This coefficient is used for the control of an automatically carried out calibration of a method.

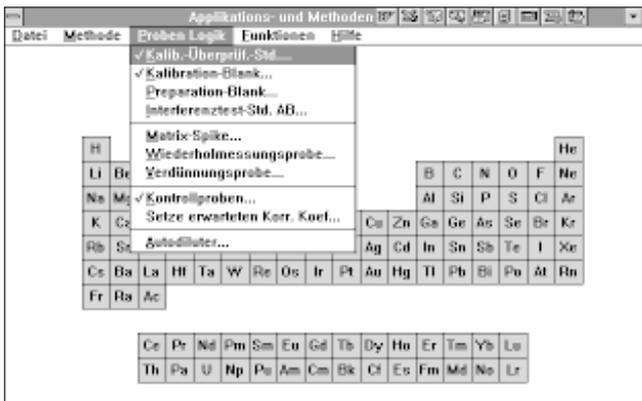


Figure 2: Window of the menu item ‚sample logic‘

Detection limits as a criterion for further actions are defined in the calibration test manager (figure 3), and when limit values are exceeded.

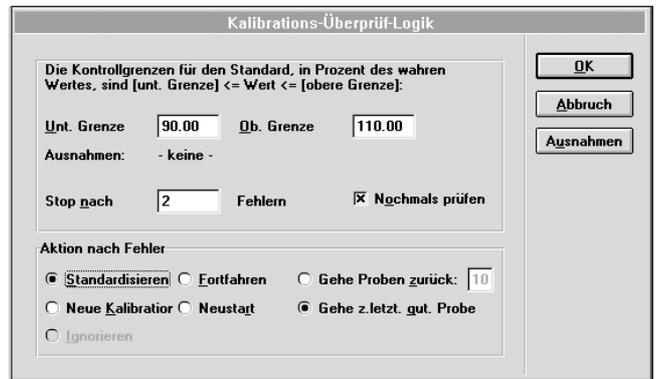


Figure 3: Calibration test logic

In the dialog in figure 3 the limit values of the analysis are set with +/- 10% relative to the defined value. When the limit value is exceeded, the analysis value is checked once again by repeated analysis. If the value is still exceeded, both actions are initiated: ‚standardization‘ and repeated analysis of all samples since the last control sample (‚go to last good sample‘). The dialog in figure 3 shows that other actions can also be specified.

In the following figure 4 an action is initiated as soon as an analysis value below the ‚low detection limit‘ of the analyzed matrix blank sample is found. After exceeding the limit values an entire calibration is carried out.



Figure 4: Dialog of the calibration blank logic

Instrument configuration of SPECTROFLAME Modula and SPECTROFLAME EOP

Optical systems:			
Optic	wave length range (nm)	Grating (grooves/mm)	Filling
polychromator	134 to 336	3600	nitrogen
polychromator	340 to 767	1800	air
Instrument parameters:			
Sample introduction			
peristaltic pump	2 mL/min		
nebulizer	Crossflow, model SPECTRO		
nebulizer pressure	3.0 bar		
nebulizer chamber	Glass, model Scott		
plasma torch	fixed torch, model SPECTRO		
Excitation unit			
R.F. power	1.3 kW		
Gas flows			
coolant gas flow	13 L/min		
auxiliary gas flow	1.5 L/min		
nebulizer gas flow	0.9 L/min		
additional gas flow	0.5 L/min		

Typical detection limits in the matrix sodium chloride

During routine analysis the use of an internal standard (Yttrium or Scandium) has proved a success. This standard is added to all samples and standards in a concentration of 1-5 ml/L. The added element for internal standardization has to be simultaneously determined with the analyt. This method compensates all effects which affect the reproduction ability and correctness from the sampling to the plasma.

The simultaneous measurement of agent and internal standard is possible with all SPECTROFLAME ICP's.

Table 1 shows typical detection limits based on the crystalline product NaCl. Using the SPECTROFLAME MODULA for analysis, standard solutions and samples are prepared with a matrix concentration of 200 g/l. The analysis with SPECTROFLAME EOP requires a matrix concentration of 100 g/l. These values represent the best possible concentrations for both, to guarantee trouble-free routine analytic processes and to achieve the lowest detection limits applicable to the solid material.

Table 1: Detection limits in sodium chloride for the SPECTROFLAME MODULA and the SPECTROFLAME EOP (compared to proposed application ranges of ESPA)

Ele- ment	Wavelength (nm)	MODULA DL (3s) (mg/kg)	EOP DL (3s) (mg/kg)	application range according to the proposal of ESPA (mg/kg)
Al	167.080	0.006	0.0015	0.1 - 30
Br	157.480	6	4	
Br	163.300	9	6	
Ca	393.366	0.005	0.001	0.02 - 30
Cd	226.502	0.025	0.005	0.1 - 30
Cr	267.716	0.031	0.009	
Cu	324.754	0.02	0.007	0.01 - 30
Fe	259.940	0.023	0.007	0.01 - 30
I	161.760	0.5	0.35	
K	766.491	0.3	0.01	
Mg	279.550	0.0015	0.001	0.02 - 30
Mn	257.610	0.007	0.0015	0.02 - 30
Ni	231.604	0.038	0.015	0.2 - 30
Pb	220.353	0.120	0.076	2 - 30
S	180.730	0.045	0.044	
Sr	407.771	0.0023	0.00067	0.02 - 30
Zn	231.860	0.0027	0.0020	0.1 - 30

To calculate the detection limits for solutions, the column 'MODULA' has to be divided by 5, the column 'EOP' by 10.

SUMMARY

Table 1 shows the suitability of the SOP (MODULA) when analyzing high-purity NaCl-solutions in routine work. Other applications like the analysis of sea water (typical salt content 3%) require the EOP: the detection limits are much better for this application.

The specialty of the SPECTROFLAME ICP is its suitability to routine work with high salt contents. Additionally the very low detection limits of the analysis line in the UVV-spectral range must be underlined. The NaCl matrix produces very much scattered light, but this affects only at a very low level the spectral background in the vicinity of the observed analysis lines. This means in practice that the relation between analysis line and spectral background has a very low deterioration level compared when used with pure water solutions. An example of the very low influence of the NaCl matrix (10%) is shown in figure 5 with the spectral background of the analysis line Al 167.080 nm in comparison to pure water.

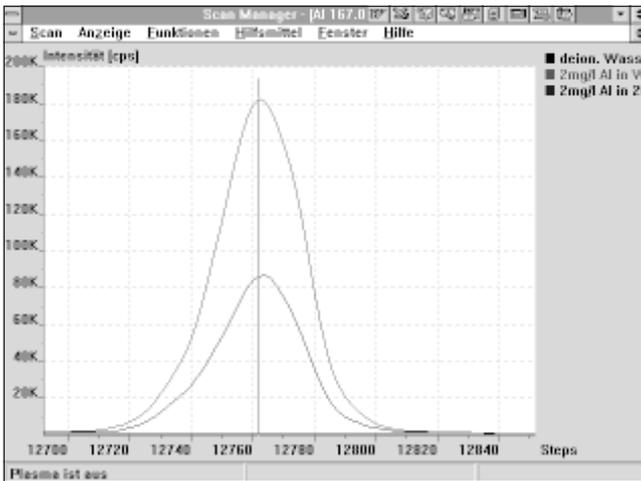
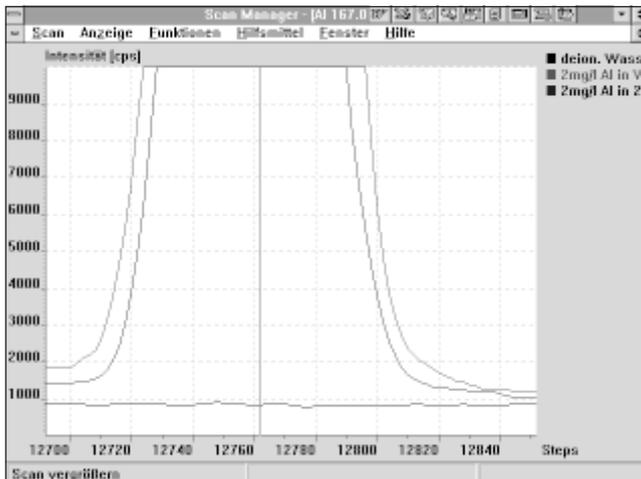


Figure 5: Spectral vicinity of the analysis line Al 167.080 nm, concentration 2 mg/l Al

- aqueous medium (flat line at the bottom)
- aqueous medium + 2 mg/l Al (topmost/outer curve)
- 20% NaCl solution + 2 mg/l Al (middle curve)

Figure 6: Magnification of figure 5, spectral vicinity of



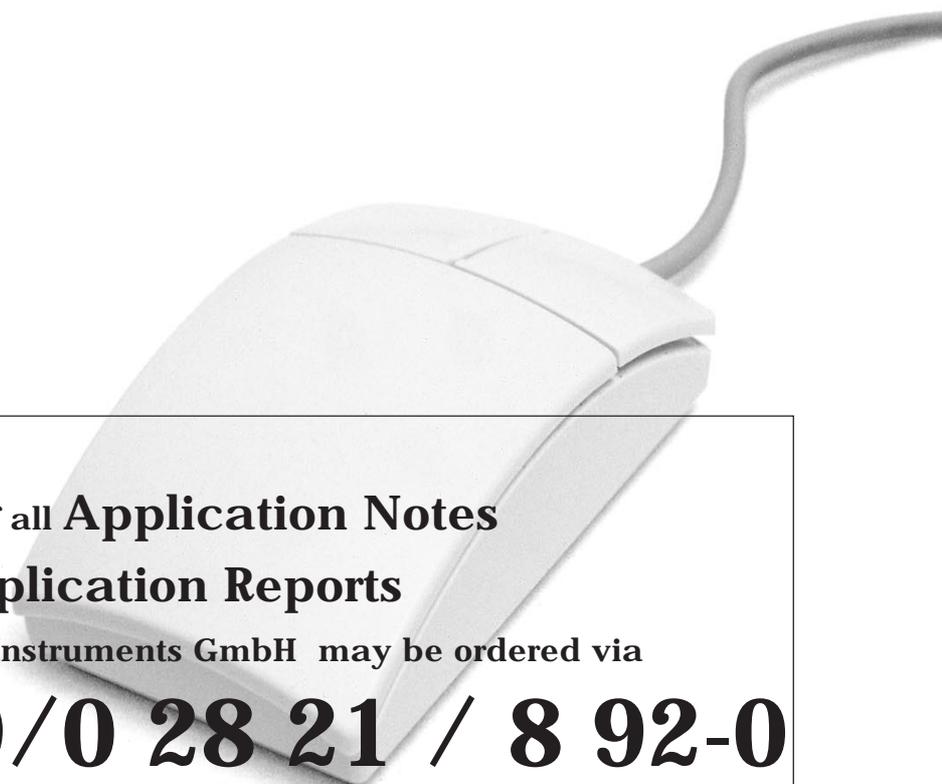
the analysis line Al 167.080 nm, concentration 2 mg/l Al

- aqueous medium (flat line at the bottom)
- aqueous medium + 2 mg/l Al (topmost/outer curve)
- 20% NaCl solution + 2 mg/l Al (middle curve)

As shown in figures 5 and 6, the spectral background in the vicinity of the analysis line Al 167.080 nm is virtually not influenced by the 20% NaCl matrix. The observed net intensity of 2 mg/l Al decreases by about 50% with the same instrument parameters: this is due to the influence of the matrix on the efficiency of the nebulizer and the plasma conditions. Optimizing the plasma parameter 'power' the net signal can be improved [3].

All SPECTROFLAME ICP's equipped with a software version (2.20 can be coupled with an ion chromatograph, which can be used for both, to enrich trace elements and to separate at the same time the matrix component (here: NaCl), [1, 2]. Coupled, the SPECTROFLAME ICP works as optical emission detector and records simultaneously the transient signals of the single elements. The analysis and evaluation of the peak areas may be performed automatically, the ion chromatograph (DIONEX Chelation) is controlled by the Spectrometer.





An overview of all **Application Notes**
and **Application Reports**
of SPECTRO Analytical Instruments GmbH may be ordered via
Tel.-Nr. +49/0 28 21 / 8 92-0
or visit SPECTRO Analytical Instruments online:
www.spectro-ai.com