

Sodium Chloride - Analytical Standard



Determination of Elements Emission Spectrometric Method (IPC-OES)

EUsalt/AS 015-2015
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1. SCOPE AND FIELD OF APPLICATION

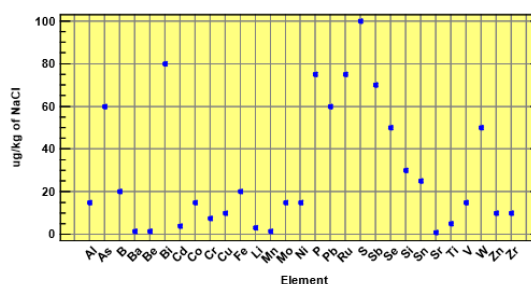
The present EUsalt Analytical Standard describes an inductively coupled plasma optical emission spectrometry method for the determination of 27 elements soluble in diluted acid, in sodium chloride. The limit of detection (LOD) for each element, determined in an inter-laboratory study is given in Table 1/Figure 1:

Table 1: Limits of Detection (LOD; reference (4))

Element	LOD, µg/kg of NaCl	Element	LOD, µg/kg of NaCl
Al	15	Mo	15
As	60	Ni	15
B	20	P	75
Ba	1.5	Pb	60
Be	1.5	Ru	75
Bi	80	S	100
Ca	not relevant	Sb	70
Cd	4	Se	50
Co	15	Si	30
Cr	7.5	Sn	25
Cu	10	Sr	1

Element	LOD, µg/kg of NaCl	Element	LOD, µg/kg of NaCl
Fe	20	Ti	5
K	(2 mg/kg)	V	15
Li	3	W	50
Mg	not relevant	Zn	10
Mn	1.5	Zr	10

Figure 1: Plot of the LOD-values from Table 1



2. REFERENCES

- (1) ISO/CD 12235 – General guidelines for inductively coupled plasma emission spectrometry.
- (2) AkzoNobel – RGL F 99131 (December 1999): Final Research Report: The determination of 26 elements in NaCl.
- (3) AkzoNobel – CAP F06017 (December 2006): Final Research Report: Determination of Pb and S in NaCl.
- (4) AkzoNobel – M12099/12104 (December 2012): Memorandum: Round robin test on NaCl
- (5) AkzoNobel – M11056 (November 2011): Memorandum: Round robin study on Salt-2011. Results, plots & statistics.

3. PRINCIPLES

Dissolution of the sample in diluted nitric acid and direct nebulisation of the acid solution into an inductively coupled argon plasma sustained by a high frequency. Measurement of the radiation emitted at a correction.

Note: The use of a reference element (internal standard), such as scandium, yttrium or cobalt, may improve the quality of the results, especially using a simultaneous spectrometer. Every mention of this optional reagent (here *scandium*) is stated in italics and in brackets.

4. REAGENTS

All reagents shall be of recognized analytical grade and the water used shall conform to grade 2 purity in accordance with EN ISO 3696.

4.1. Nitric acid, $\rho \approx 1.40$ g/ml, 65 % (m/m)

4.2. Sodium chloride solution, $\beta(\text{NaCl}) = 250$ g/l

Dissolve 250 g of very pure NaCl (see note) in water and transfer to a 1000 ml volumetric flask. Make up to the mark and mix.

Note: A very pure salt is a salt with elemental impurities at least three times lower than the respective limits of detection given in Table 1.

[4.3. Scandium (reference element) solution, $\beta(\text{Sc}) = 50$ mg/l

Transfer 50 ml of a scandium stock solution $\beta(\text{Sc}) = 1000$ mg/l and 10 ml nitric acid (4.1.) into a 1000 ml volumetric flask. Make up to the mark and mix.]

4.4. Element stock solution, β (each element) = 1000 mg/l certified commercial solutions.

Note: The stock solution has to be certified not only for the element itself but also for the other analyte elements (impurities).

4.5. Argon, pressure not less than 7 bar. The argon used may be compressed or liquefied gas.

5. APPARATUS

Usual laboratory equipment (see 9.1) and:

5.1. ICP, inductively coupled plasma emission spectrometer fitted with a nebulizer and a torch for high salt concentrations and with an argon humidifier filled with water. This instrument may measure simultaneously and/or sequential. The specifications and operating conditions used with most spectrometers are given in appendix 1.

6. SAMPLING AND SAMPLES

A test sample of about 500 g should be taken for analysis, ensuring that it is representative of the whole batch.

7. PROCEDURE

7.1. Test portion (see 9.2)

Weigh, to the nearest 0.1 g, about 10 g of the test sample.

7.2. Test sample solution

Transfer the test portion (7.1) and water to a 100 ml volumetric flask and stir to dissolve. Add 1 ml nitric acid (4.1.), [5 ml of scandium solution (4.3.)], make up to the mark and mix.

7.3 Calibration and verification solutions (see 9.2)

Calibration solution No. 1 is the blank calibration solution and contains 1 ml of nitric acid (4.1.). Transfer 40 ml of sodium chloride solution (4.2.), 1 ml of nitric acid (4.1.), [5 ml of scandium solution (4.3.)] and the volumes of each stock solution (4.4.) to obtain the concentrations indicated in table 2, into a series of further three 100 ml volumetric flasks to obtain the calibration solutions No. 2 – 4. Make up to the mark and mix.

Table 2: Calibration solutions

Calibration solution No.	Concentration of NaCl (g/l) (see 9.2)	Concentration of elements mg/l
1 ⁽¹⁾	0	0
2 ⁽²⁾	100	2.5 ⁽⁴⁾
3	100	5.0 ⁽⁵⁾
4 ⁽³⁾	100	5.0 ⁽⁵⁾
⁽¹⁾ blank calibration solution ⁽²⁾ linearity verification solution ⁽³⁾ control calibration solution prepared with different pipettes, flasks and if possible with different stock solutions ⁽⁴⁾ except for K: 25 mg/l, SO ₄ : 50 mg/l ⁽⁵⁾ except for K: 50 mg/l, SO ₄ : 100 mg/l		

7.4 Determination

7.4.1 Settings of the apparatus

Set all instrumental parameters of the optical emission spectrometer (5.1.) in accordance with the operating manual of the instrument's manufacturer.

Prepare the analytical procedure including the lines shown in appendix 2 (or lines with similar sensitivity and free from interferences), with background correction and concentrations of calibration solutions 1 and 3 described in (7.3.) [and applying the reference technique].

7.4.2. Spectrometric measurements

Repeat the measurements for at least five integration periods.

If necessary, rinse with the blank calibration solution (solution 1) after each solution.

Calibrate the instrument with the calibration solutions 1 and 3 (7.3.).

Control and check the linearity of the calibration curve by measurement of the following calibration solutions

(7.3) considered as unknown solutions:

- solution 3,
- solution 1,
- solution 1,
- solution 2,
- solution 4,
- solution 3.

Note: If the calibration function does not appear to be a linear one, the corresponding calibration range should be decreased.

Continue the measurements in the following order:

- solution 3 (7.3.),
- solution 1 (7.3.),
- solution 1 (7.3.),
- test sample solution(s) (7.2.),
- solution 3 (7.3.),
- solution 1 (7.3.),
- solution 1 (7.3.).

Note: Five to ten test sample solutions may be analysed consecutively, provided the stability of the measurements is sufficient.

8. EXPRESSION OF RESULTS

8.1. Evaluation

If necessary, correct the results obtained with the test sample solution for drift:

- For baseline drift by interpolating in time between both second measurements (the first may be cross-contaminated) of the blank calibration solution (solution 1),
- For sensitivity drift by interpolating in time between the corrected measurements for baseline drift of the control solution 3.

The element content of the sample, $\omega_{(\text{Element})}$ in micrograms per kilogram of sodium chloride is given by the formula:

$$\omega_{(\text{Element})} = \frac{100}{m} \times \beta_{(\text{Element})} \times 1000$$

where

- m is the mass in grams of the test portion (7.1.),
- β is the corrected concentration of element, in mg/l in the test sample solution (7.2.).

Report the results as given in the next Table:

Element concentration in $\mu\text{g/kg}$ of NaCl	
< LOD	as < LOD
LOD - 10	to the nearest 0.1 $\mu\text{g/kg}$ of NaCl
10 - 100	to the nearest 1 $\mu\text{g/kg}$ of NaCl
> 100	to the nearest 10 $\mu\text{g/kg}$ of NaCl

8.2. Repeatability and reproducibility

Analyses carried out on five samples, containing the 27 elements in different concentrations, by 16 laboratories, gave the following statistical results, each laboratory performed three replicates under repeatability conditions:

Table 3: Results of the inter-laboratory study
(For details see (2))

Blue shaded values are below **LOQ** ≈ 3 times LOD. The dimension in this Table 3 is **mg** element/kg of NaCl.

Sample	ω	Sr	Sr	r	R
Aluminium					
1	0.02	0.034	0.034	0.10	0.10
2	0.44	0.050	0.060	0.14	0.17
3	8.32	0.145	0.482	0.41	1.36
4	2.16	0.056	0.169	0.16	0.48
5	16.12	0.473	1.174	1.34	3.32
Arsenic					
1	0.08	0.124	0.216	0.35	0.61
2	0.84	0.106	0.181	0.30	0.51
3	2.04	0.079	0.166	0.22	0.47
4	20.76	0.312	1.120	0.88	3.17
5	8.16	0.210	0.577	0.59	1.63
Barium					
1	0.000	0.003	0.026	0.01	0.07
2	0.09	0.036	0.045	0.10	0.13
3	0.40	0.009	0.047	0.02	0.14
4	2.08	0.018	0.086	0.05	0.12
5	7.92	0.082	0.343	0.23	0.97
Beryllium					
1	0.01	0.006	0.031	0.02	0.09
2	0.10	0.048	0.077	0.14	0.22

Sample	ω	Sr	Sr	r	R
3	0.42	0.010	0.044	0.03	0.12
4	2.09	0.024	0.097	0.07	0.28
5	7.71	0.280	0.564	0.79	1.60
Bismuth					
1	-0.10	0.137	0.186	0.39	0.52
2	0.88	0.239	0.284	0.68	0.80
3	1.84	0.148	0.192	0.42	0.54
4	20.36	0.538	1.717	1.52	4.86
5	7.96	0.359	0.797	1.02	2.26
Calcium					
1	0.03	0.001	0.004	0.004	0.01
2	0.68	0.006	0.030	0.02	0.08
3	1.00	0.013	0.047	0.04	0.13
4	2.68	0.028	0.121	0.08	0.34
5	8.36	0.130	0.434	0.37	1.230
Cadmium					
1	0.02	0.009	0.021	0.02	0.06
2	0.40	0.018	0.023	0.05	0.05
3	8.00	0.107	0.196	0.30	0.55
4	2.08	0.030	0.106	0.08	0.30
5	15.48	0.318	0.822	0.90	2.33

Sample	ω	S _r	S _R	r	R
Cobalt					
1	0.00	0.021	0.032	0.06	0.09
2	0.40	0.024	0.031	0.07	0.09
3	7.96	0.155	0.268	0.44	0.76
4	2.00	0.034	0.062	0.10	0.18
5	15.60	0.320	0.920	0.90	2.60
Chromium					
1	0.00	0.010	0.028	0.03	0.08
2	0.39	0.014	0.033	0.04	0.09
3	7.96	0.080	0.258	0.23	0.73
4	2.00	0.031	0.074	0.09	0.21
5	15.44	0.378	0.971	1.07	2.75
Copper					
1	0.00	0.012	0.024	0.04	0.07
2	0.38	0.011	0.022	0.03	0.06
3	7.80	0.086	0.388	0.24	1.10
4	1.92	0.030	0.104	0.08	0.30
5	14.96	0.239	0.970	0.68	2.74
Iron					
1	0.01	0.024	0.034	0.07	0.10
2	0.44	0.024	0.030	0.07	0.09

Sample	ω	S _r	S _R	r	R
3	8.20	0.113	0.282	0.32	0.80
4	2.08	0.026	0.062	0.07	0.18
5	15.88	0.271	0.619	0.77	1.75
Potassium					
1	84.00	1.600	6.100	4.00	17.00
2	96.00	1.400	6.600	4.00	19.00
3	168.00	3.300	8.300	9.00	24.00
4	104.00	2.200	4.000	6.00	11.00
5	236.00	9.800	15.000	28.00	43.00
Magnesium					
1	0.06	0.120	0.200	0.04	0.06
2	3.72	0.316	0.155	0.09	0.44
3	4.00	0.568	0.176	0.16	0.50
4	5.84	0.056	0.350	0.16	0.99
5	11.48	0.364	0.740	1.03	2.09
Manganese					
1	0.00	0.001	0.004	0.004	0.01
2	0.08	0.002	0.003	0.004	0.01
3	0.40	0.007	0.027	0.02	0.04
4	2.08	0.022	0.068	0.06	0.19
5	7.80	0.170	0.405	0.48	1.15

Sample	ω	Sr	SR	r	R
Molybdenum					
1	0.00	0.026	0.030	0.07	0.08
2	0.40	0.023	0.054	0.06	0.15
3	8.12	0.096	0.278	0.27	0.79
4	2.04	0.042	0.084	0.12	0.24
5	15.80	0.303	0.756	0.86	2.14
Nickel					
1	-0.04	0.026	0.132	0.08	0.38
2	0.37	0.022	0.108	0.06	0.30
3	8.04	0.058	0.251	0.16	0.71
4	2.00	0.039	0.146	0.11	0.41
5	15.64	0.296	0.628	0.84	1.78
Lead **)					
1	0.004	0.05	0.082	0.14	0.23
2	0.92	0.064	0.204	0.18	0.57
3	1.89	0.064	0.207	0.18	0.58
Antimony					
1	0.01	0.100	0.100	0.28	0.28
2	0.76	0.169	0.212	0.48	0.60
3	2.20	0.233	0.840	0.66	2.38
4	18.96	0.529	1.503	1.50	4.25

Sample	ω	Sr	SR	r	R
5	7.92	0.338	1.327	0.96	3.76
Selenium					
1	0.02	0.070	0.082	0.20	0.23
2	0.76	0.094	0.106	0.26	0.30
3	1.96	0.107	0.113	0.30	0.32
4	20.28	0.315	0.710	0.89	2.01
5	7.88	0.266	0.370	0.75	1.05
Silicon					
1	0.08	0.069	0.100	0.20	0.28
2	0.84	0.081	0.196	0.23	0.56
3	2.16	0.138	0.194	0.39	0.55
4	19.08	0.652	1.382	1.85	3.91
5	7.80	0.285	0.533	0.81	1.51
Tin					
1	0.01	0.097	0.121	0.27	0.34
2	0.80	0.158	0.185	0.45	0.52
3	1.84	0.138	0.218	0.39	0.62
4	19.24	0.254	1.103	0.72	3.12
5	7.48	0.163	0.429	0.46	1.21
Strontium					
1	0.03	0.001	0.004	0.00	0.01

Sample	ω	s_r	SR	r	R
2	0.68	0.006	0.030	0.02	0.08
3	1.00	0.013	0.047	0.04	0.13
4	2.68	0.028	0.121	0.08	0.34
5	8.36	0.130	0.434	0.37	1.23
Titanium					
1	0.01	0.006	0.008	0.02	0.02
2	0.40	0.020	0.029	0.06	0.08
3	7.92	0.064	0.342	0.18	0.97
4	2.00	0.032	0.081	0.09	0.23
5	15.40	0.262	0.809	0.74	2.29
Vanadium					
1	0.00	0.017	0.039	0.05	0.11
2	0.40	0.014	0.027	0.04	0.08
3	8.00	0.046	0.161	0.13	0.46
4	2.00	0.024	0.048	0.07	0.14
5	15.68	0.186	0.278	0.52	0.79
Zinc					
1	0.02	0.018	0.021	0.05	0.06
2	0.40	0.034	0.052	0.10	0.15
3	8.08	0.092	0.330	0.26	0.93
4	2.04	0.038	0.098	0.11	0.28

Sample	ω	s_r	SR	r	R
5	15.56	0.407	0.814	1.15	2.30
Zirconium*)					
2	0.50	0.037	0.120	0.10	0.34
3	8.60	0.152	0.539	0.43	1.52
4	2.20	0.094	0.252	0.26	0.71
5	17.08	0.208	1.003	0.59	2.84
Sulphate **)					
1	46	0.818	1.55	2.29	4.33
2	439	5.964	11.2	16.7	31.4
3	940	8.893	15.6	24.9	43.7

*) Sample 1 was omitted because of statistical reasons

**) ILS conducted 2006 with 13 laboratories participating

8.3 Expression of results

The limit of detection (LOD) –the lowest concentration of the element which can be detected with a coefficient of variation of 30%- is calculated based on the repeatability standard deviation s_r of each element near the estimated LOD. (For details see report (4)).

9. REMARKS

9.1. All vessels (glassware, polyethylene-, polypropylene- and PTFE-flasks) should be washed successively with hydrochloric acid, $c(\text{HCl}) \approx 6 \text{ mol/l}$ and water.

9.2. Use the highest concentration of NaCl acceptable to the spectrometer and correct the calibration- and verification-solutions accordingly.

9.3. In 2006 another ILS was conducted by 13 laboratories in order to improve the LOQ of lead and to incorporate sulphur in the method.

9.4. In 2012 an ILS was conducted by 16 laboratories in order to statistically establish the LOD (limit of detection) of the ICP-OES method for 32 elements.

9.5. In 2011 an ILS was conducted by 17 laboratories (13 ICP-ES; 1 ICP-MS; 1 AAS; 1 stripping voltammetry; 1 unknown) on Pb, Cd, Cu, As and Zn in brine, 200 g NaCl/l, spiked with 0.10 mg/l and 0.20 mg/l of each element. Overall result expressed in 95 % confidence interval:

Brine-2011-04: 39 observations; 105.2 ± 2.88 g As/l.
Brine-2011-05: 36 observations; 208.4 ± 2.85 g As/l.
Brine-2011-04: 37 observations; 100.8 ± 0.93 g Cd/l.
Brine-2011-05: 37 observations; 202.8 ± 2.21 g Cd/l.
Brine-2011-04: 42 observations; 101.5 ± 1.68 g Cu/l.
Brine-2011-05: 39 observations; 206.9 ± 3.79 g Cu/l.
Brine-2011-04: 37 observations; 105.6 ± 3.09 g Pb/l.
Brine-2011-05 : 37 observations; 207.2 ± 5.17 g Pb/l.
Brine-2011-04: 37 observations; 102.1 ± 1.56 g Zn/l.
Brine-2011-05: 37 observations; 207.0 ± 3.41 g Zn/l.

See report 5 for more details & statistics.

Appendix 1

Typical operation conditions for most ICP spectrometers *)

Argon flows (l/min)	
- plasma	12 – 15
- auxiliary	≈ 1.5
- nebulizer	≈ 0.7
Sample flow (ml/min)	≈ 1.5
RF power (W)	1000 - 1250
Integration time (sec)	
- simultaneous	≈ 10
- sequential	≈ 3

*) Check for use with high salinity solutions

Appendix 2

Typical Wavelength per element

Element	Wavelength (nm)	Element	Wavelength (nm)
Al	167.081	Mo	202.030
	396.152	Ni	221.647
As	189.042		231.604
	193.696	P	177.495
B	249.773	Pb	168.220
Ba	455.403		220.353
Be	313.042	Ru	240.272
	313.107	S	182.034
Bi	223.061		180.731
Ca	317.933	Sb	217.581
	393.366	Se	196.026
Cd	214.438	Si	251.611
	228.802	Sn	189.980
Co	228.616	Sr	407.771
Cr	267.716	Ti	334.940
Cu	324.754	V	292.402
Fe	238.204		310.230
	259.940	W	207.911
K	766.490	Zn	213.856
Li	670.780	Zr	343.823
Mg	279.553	Sc	424.683
	280.270	(reference element)	361.384
Mn	257.610		

Note: Other lines with similar sensitivity and free from interferences may be used.