

Application Note

► Determination of organic and inorganic ions in beer



Category	Food
Matrix	Beer
Method	IC
Keywords	Beer, Ion chromatography, organic and inorganic anions
Analytes	Chloride, Nitrate, Phosphate, Sulphate, Oxalate
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Summary

The analysis of Oxalate and other anions in Beer with excellent detection limits can be realized easily and reasonably with an isocratic HPLC system in combination with the conductivity detector.

Introduction

In many agriculture derivate products the control of the amount of Oxalate is highly recommended and required. In many agriculture products Oxalate is found as insoluble Calcium Oxalate. Calcium, which is an essential mineral for the human body is not easily consumed if it exists in the Calcium Oxalate form. Consequently, the quantification of oxalate in consumable products is absolutely essential.

The presented method is based on ion exchange chromatography which can easily be applied in analytical laboratories to analyse anions, especially Oxalate in beer.

In suppressor-based Ion chromatography an anion exchange column with a high conductivity mobile phase is used. A suitable polymer anion exchange column, which is packed with a methacrylate-based anion exchanger, can be used to separate Oxalate from other anions. A suppressor is required to suppress the background conductivity of the mobile phase and to enhance the analysis signal. A sensitive determination of Oxalate in Beer in the range of 0,4 mg/l up to 40 mg/l is realizable.

Experimental Sample Preparation

The sample preparation is very simple and only needs n-octanol. With a drop of this alcohol the Beer sample will be degassed in an ultrasonic bath. The sample needs to be filtered (0.45 µm syringe filter unit) and can be diluted for 10 times before injecting.

Experimental Preparation of Standard Solution

Single standard solutions with a concentration of 1 mg/ml will be produced.

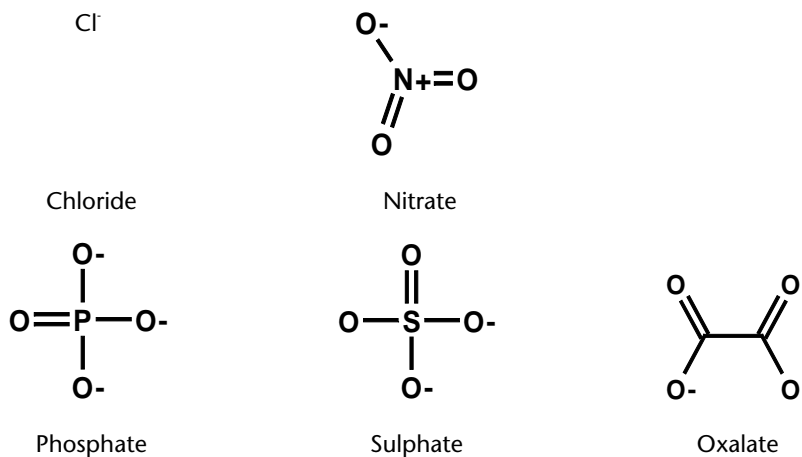
The following volumes of the different standard solutions will be transferred into a 500 ml calibrated flask and filled with pure water to prepare the standard solution a.

Chloride	6 ml (0.012 mg/ml)	Nitrate	20 ml (0.04 mg/ml)
Phosphate	50 ml (0.1 mg/ml)	Sulphate	30 ml (0.06 mg/ml)
Oxalate	88 ml (0.0176 mg/ml)		

The calibration solutions will be prepared from the mixed standard solution a in a 100 ml calibrated flask with the listed volumes:

Solution	Volume [ml]	Chloride [mg/l]	Nitrate [mg/l]	Phosphate [mg/l]	Sulphate [mg/l]	Oxalate [mg/l]
1	2.5	0.3	1.0	2.5	1.5	4.40
2	5	0.6	2.0	5.0	3.0	8.80
3	10	1.2	4.0	10.0	6.0	17.6
4	20	2.4	8.0	20.0	12.0	35.2

Chemical Structures



Method Parameters

Column	Anion 100 x 4,6 mm
Eluent	isocratic 0.85 mM NaHCO ₃ ; 0.9 mM Na ₂ CO ₃
Flow rate	1.2 ml/min
Injection volume	100 µl
Column temperature	40 °C
System pressure	approx. 53 bar
Detection	Conductivity
Run time	20 min

Results

The isocratic separation of an anion standard solution containing Oxalate using suppressor-based IC method is presented in Fig. 1. The demanded limit of determination of Oxalate in Beer of 0.4 mg/l can easily be realised.

The calculated linear range of the Oxalate determination goes up to 35 mg/l with excellent correlation. Figure 2 shows the separation of Oxalate and other anions in a German Beer sample. The concentration of oxalate in the investigated beer sample could be determined with 9.94 mg/l. This is a good corresponding result comparing to literature. Normal concentration range in Beer varies from 8 mg/l up to 34 mg/l [1]. Additionally the chromatogram shows that also other anions than Oxalate can be positive detected. The quantification results for Chloride, Nitrate, Phosphate and Sulphate are also listed in Table 1.

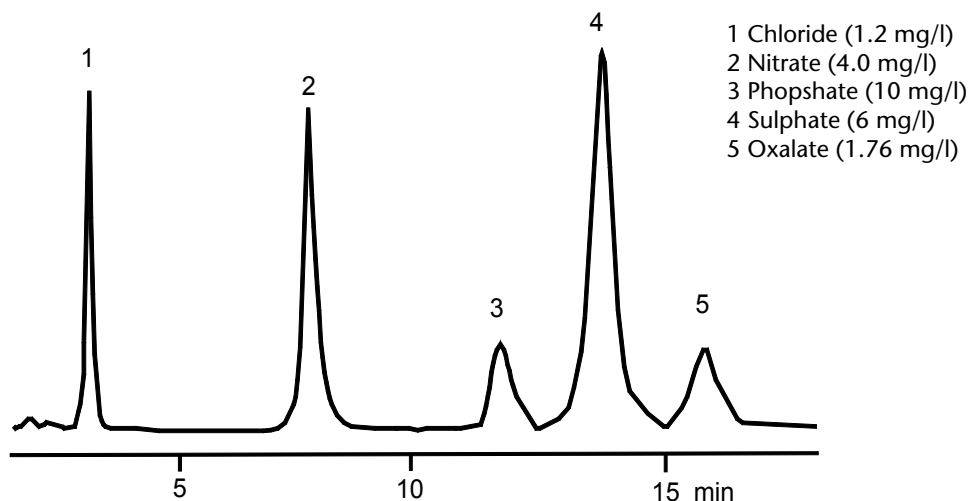


Fig. 1

Chromatogram of the anion standard solution 3

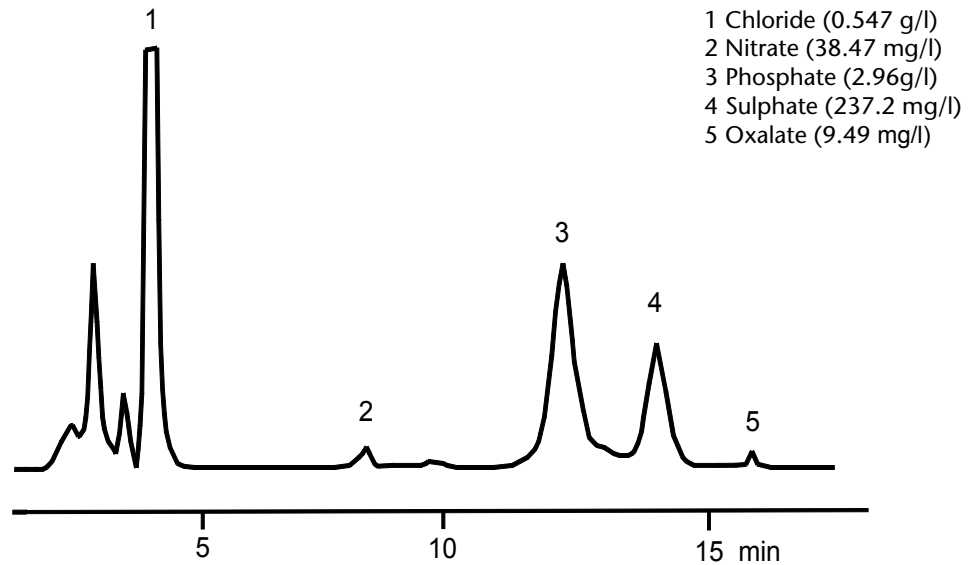


Fig. 2
 Chromatogram of a German Beer sample (1:10 dilution)

Table 1

Substance	t_r (min)	Area	mg/l	LOD (mg/l)
Chloride	3.800	173682470	(547.68)*	0.05
Nitrate	8.067	7395717	38.47	0.16
Phosphate	12.050	111949521	(2955.13)*	0.49
Sulphate	13.933	57461389	237.16	0.18
Oxalate	15.833	1968789	9.49	0.11

(* out of linear range)

Method Performance

Limit of detection	mg/l range (S/N =3)
Linearity (r^2)	0.999885-0.99993
Linearity range	0.3 to 35 mg/l
Retention time precision*	< 0.2 % RSD
Peak area precision*	< 3 % RSD

*repeatability calculated over 10 replicate runs

Conclusion

The presented application to analyse Oxalic acid in Beer and other suitable matrices in Ion Chromatography Mode is easy to realize. With the described Knauer system configuration a sensitive, flexible and reliable conductivity detection of Oxalate in beer samples can be performed. The suppressor-based method is strongly recommended for sensitive detection of organic or inorganic anions in the part-per-billion level.

References

- [1] D. Madigan, I. McMurrugh, and M. R. Smyth, 1994 "Determination of oxalate in beer and beer sediments using Ion Chromatography" (VOL 52 PG 134 1993). Journal of the American Society of Brewing Chemists, 52, pp171-171.

Physical Properties of recommended Column

A polymer based anion exchanger with 7 µm particle size is compatible with common IC mobile phases: carbonate, bicarbonate, p-hydroxybenzoic acid, phthalic acid, succinic acid, and sodium octane sulfonate. The anion exchange material is characterized by methacrylate polymer with quarternary ammonium groups.



Stationary phase	Allsep Anion IC column
Dimensions	100 x 4.6 mm
Order number	B90

Recommended Instrumentation



This application requires an isocratic HPLC system equipped with degasser, autosampler, column oven, and conductivity detector. Please contact KNAUER to configure a system that's perfect for your needs.

Description	Order No.
Smartline Pump 1000, incl. 10 ml pump head	A50303
Smartline Manager 5000 with degasser and Interface	A5312
Autosampler 3900	A1508
Smartline Column Oven 4000	A5300
Conductivity Detector	A1252-1
Suppressor Kit for isocratic mode	A09412
ChromGate Software	A1493

Author

Silvia Marten, Head of Columns and Applications Department, KNAUER

Contact Information

Wissenschaftliche Gerätebau
Dr. Ing. Herbert Knauer GmbH
Hegauer Weg 38 · D-14163
Berlin, Germany

Tel: +49 (0)30 / 809727-0
Fax: +49 (0)30 / 8015010
E-Mail: info@knauer.net
Internet: www.knauer.net