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Anion Suppressor Ion Chromatograph HIC-ESP

Application News

Analysis of Total Nitrogen and Total Phosphorus in Environmental Water According to ASTM D8001 by Ion Chromatography

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User Benefits

- Total nitrogen (TN) and Total phosphorus(TP) in environmental water can be analyzed in accordance with ASTM D8001.
- TN and TP can be measured simultaneously in a single alkaline persulfate digestion.
- The use of the ICDS™-40A suppressor in recycle mode is enabling environmental friendly analysis.

■ Introduction

In recent years, the issue of eutrophication of water quality has attracted attention. Measures against eutrophication are also included in Goal 14 of the SDGs, "Protect the Abundance of the Sea," which has become a global issue. The major cause of eutrophication is said to be phosphorus and nitrogen, which nourish phytoplankton in water. Industrial and domestic wastewater produced by human activities contains a large amount of nitrogen and phosphorus, which are discharged into rivers, leading to eutrophication. Therefore, it is essential to control the concentration of phosphorus and nitrogen in wastewater.

Ion chromatographs are widely used to analyze nitrate and phosphate ions in the environment. The sensitivity of the suppressor ion chromatograph is improved by replacing sodium ions in the eluent with hydrogen ions before detection. Figure 1 shows the flow diagram of an ion chromatograph HIC-ESP for anion analysis equipped with an electro dialyzable suppressor.

In this report, we introduce examples of analysis of total nitrogen (TN) and total phosphorus (TP) in environmental water in accordance with ASTM D8001 using the anion suppressor ion chromatograph HIC-ESP.

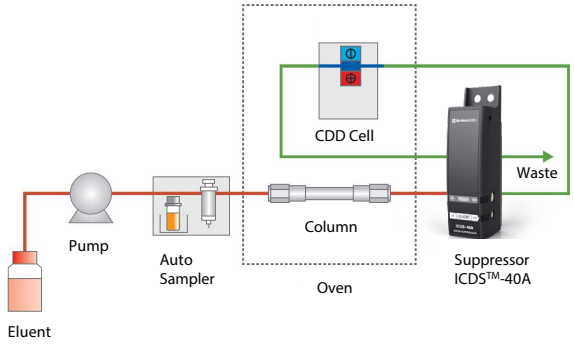

Fig. 1 The Suppressor Ion Chromatograph Flow Chart for Anion Analysis

The Standard D8001 of American Society for Testing and Material (ASTM), is a test method for TN, TP and for total Kjeldahl nitrogen (TKN) by calculation in water and wastewater by ion chromatography.

In Standard D8001, TN and TP can be analyzed by alkaline persulfate digestion followed by ion chromatography and TKN is determined by the calculation. TKN is calculated by subtracting the concentrations of nitrate nitrogen (NO_3-N) and nitrite nitrogen (NO_2-N) in the undigested sample from the concentration of nitrate nitrogen (NO_3-N) in the digested sample.

Total Organic Carbon Analysis (TOC) is mainly used for the measurement of TN and TP. However, TOC requires digestion of TN and TP for each sample. Furthermore, it is impossible to measure phosphate ions and nitrate ions simultaneously because another molybdenum blue method is required for the digested phosphate ions. The ASTM D8001 method has the advantage of using ion chromatography to simultaneously measure TN and TP in a single sample digestion.

■ Analytical Conditions

Table 1 shows the analytical conditions.

Table 1 Analytical conditions

Column	Shodex SI-52 4E (250 mm×4.0 mm I.D., 5 µm)
Guard column	Shodex SI-92G (10 mm×4.6 mm I.D., 9 µm)
Mobile phase	3.6 mmol/L sodium carbonate
Flow rate	0.8 mL/min
Column temp.	45 °C
Injection volume	200 µL
Vial	Shimadzu Vial, LC, 4 mL, Polypropylene*1
Detection	Conductivity

*1 P/N：228-31537-91

■ Analysis of Standards and Calibration Curve

6 calibration standards were prepared in the concentration range of 10 to 300 µg/L and the calibration curve was prepared by linear regression. The coefficient of determinations are summarized in Table 2. Figure 2 shows the chromatogram for STD 4 (100 µg/L each).

Table 2 The coefficient of correlations

Component	NO_2-N	NO_3-N	PO_4-P
Coefficient of determination (r^2)	0.9997	0.9999	1.0000

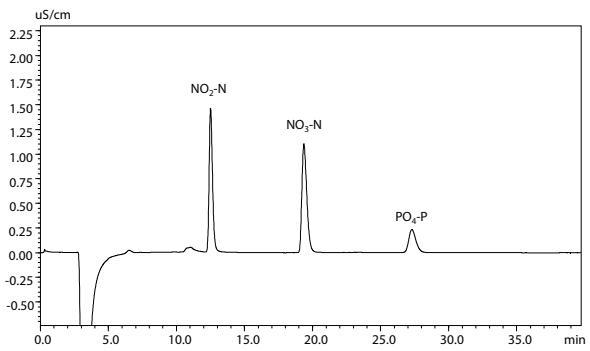

Fig. 2 The chromatogram of mixed standard solution (STD 4: 100 µg/L each)

■ Reproducibility and Method Detection Limit

To evaluate the performance of instrument, the STD1 (10 µg/L each) was measured 7 times repeatedly. Table 3 shows the results of reproducibility of retention time and peak area.

Table 3 Reproducibility of STD 1

Component	NO_2-N		NO_3-N		PO_4-P	
Replicates	Retention time (min)	Peak	Retention time (min)	Peak	Retention time (min)	Peak
1	12.32	2534	19.05	2837	26.82	805
2	12.32	2467	19.06	2756	26.84	799
3	12.32	2548	19.06	2786	26.83	803
4	12.32	2524	19.06	2693	26.86	758
5	12.33	2495	19.07	2815	26.83	810
6	12.33	2461	19.07	2822	26.83	801
7	12.33	2497	19.08	2802	26.82	793
Average	12.32	2504	19.06	2787	26.83	796
%RSD	0.04	1.33	0.05	1.76	0.05	2.21

The method detection limit (MDL) was calculated by performing 7 replicate analyses of the MDL solution according to the procedure described in ASTM D8001 and using the formula shown in Table 4. The MDL solution used a digestion blank which added 5 µg/L PO_4-P here. The continuous analysis results are shown in Figure 3, and the calculated MDL are shown in Table 5.

Table 4 Formula of MDL

$$MDL_s = t_{(n-1,\ 1-\alpha=0.99)} \times S_s$$

t=3.14, and
S_s = standard deviation of the standard the replicate (n = 7) spiked blank sample analyses.

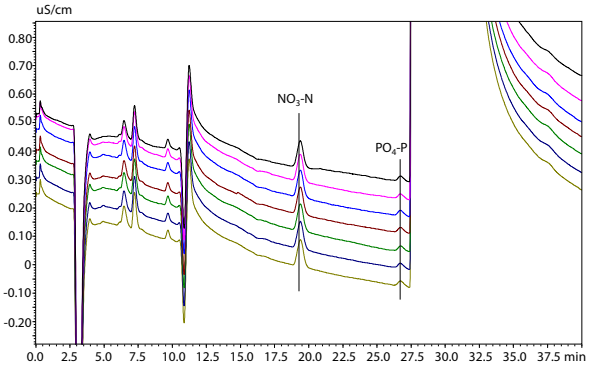

Fig. 3 Continuous analysis chromatogram (n=7)

Table 5 Analysis result of MDL (n=7)

	TN (µg/L)	TP (µg/L)
MDL-1	10.33	6.53
MDL-2	10.57	6.14
MDL-3	10.71	7.65
MDL-4	10.59	7.04
MDL-5	10.77	6.54
MDL-6	10.93	6.94
MDL-7	10.61	7.38
Average	10.64	6.89
SD	0.19	0.53
MDL (3.14 X SD)	**0.60**	**1.66**

■ Digestion and Analysis of Mixed Digest-check Sample

ASTM D8001 requires a digestion to detect TN as nitrate and TP as phosphate in the sample. Furthermore, in order to confirm the effectiveness of the digestion, we conducted spike recovery test using a mixed digest-check sample.

For digestion, the sample and alkaline persulfate digests (Potassium peroxydisulfate, low nitrogen, ACS, 99.0% min、CAS number: 7727-21-1、Alfa Aesar) were mixed in a 2:1 ratio and heated in an autoclave at 120°C for 60 minutes.

Here, we used a mixed digest-check solution. Aqueous solutions of glycine, glycerol phosphate, and glucose were weighed to obtain final concentrations of 4 mg-N/L, 1.6 mg-P/L, and 50 mg-C/L in ultrapure water. 7 replicates analyzes were performed with the mixed digested-check sample and ultrapure water was used as the digestion blank. Since the sample subjected to the above digestion contains a high concentration of sulfate ions derived from the digestion reagent, to reduce carry-over and interference with other analytical components, the sample was diluted 30 times with ultrapure water before analysis.

Figure 4 shows the chromatograms of the digestion blank and the mixed digest-check sample, and Table 6 shows the results of the spike recoveries.

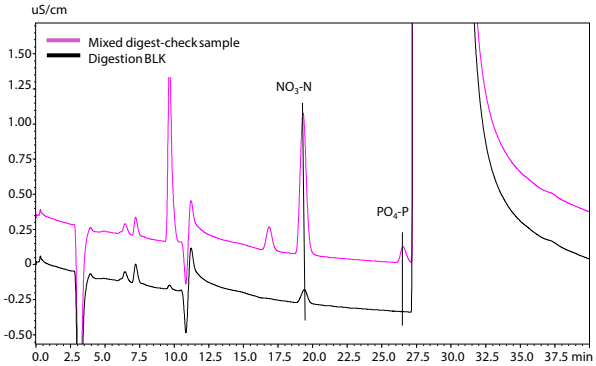

Fig. 4 The chromatogram of digestion blank and mixed digest-check sample (Diluted 30 times after digestion)

Table 6 Spike recoveries of mixed digest-check sample (n=7)

		TN	TP
Digestion blank	Average of measured concentration (mg/L)	0.012	N.D. *1
	Concentration of stock solution *2 (mg/L)	0.55	N.D.
Mixed digest-check sample	**Compounds**	**Glycine (FW: 111.5)**	**Glycerol phosphate (FW: 306.1)**
	Average of measured concentration (mg/L)	0.11	0.039
	Concentration of stock solution*3 (mg/L)	4.97	1.74
	Found concentration *4 (mg/L)	4.42	1.74
	Weight (g)	0.42	0.50
	Expected concentration *5 (mg/L)	4.22	1.62
Spike recovery (%) *6		**105.8**	**107.8**

*1 Below MDL.
*2 Multiplied the measured concentration by the dilution ratio.
*3 Multiplied the measured concentration by the dilution ratio.
*4 Subtracted the concentration of stock solution (mixed digest-check sample) from the concentration of stock solution (digestion blank).
*5 Converted to the concentration in solution.
*6 Found concentration / expected concentration * 100.

■ Analysis of Environmental Water

0.1 g/L sea water was used as the analytical sample, which was made from commercially available sea salt diluted with ultrapure water. To calculate the TKN, the digested sample and undigested sample were analyzed 3 times each. The digested sample was also diluted 30 times with ultrapure water before analysis. Furthermore, to verify the analytical accuracy, a certain amount of standard solution was added to the digested sample, 3 replicates analyzes was performed and the spike recovery was calculated.

Figure 5 shows the chromatogram of undigested and digested sample. The analysis results are shown in Table 7 and the spike recoveries are shown in Table 8. There is neither TN nor TP was found in this analysis.

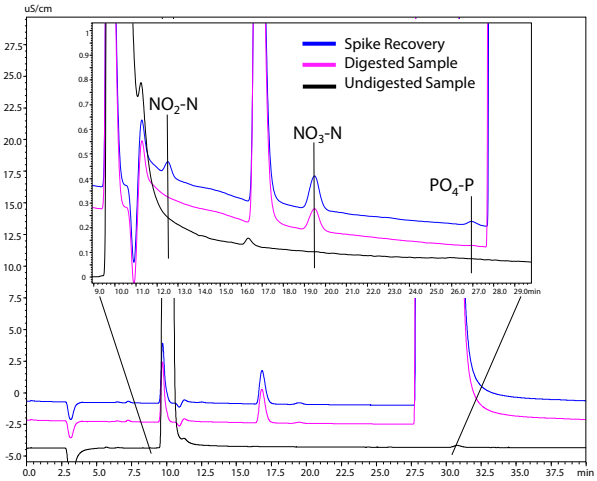

Fig. 5 The chromatogram of undigested sample, digested sample and spiked sample (Diluted 30 times after digestion)

Table 7 Analytical result of sample (n=3)

	Nitrogen (µg/L)		Phosphorus (µg/L)
Undigested sample	**NO_2-N**	**NO_3-N**	**PO_4-P**
Average of measured concentration	N.D. *1	N.D.	N.D.
Digested sample	**NO_3-N**		**PO_4-P**
Concentration of stock solution *2	0		0
TKN *4	0		---

*1 Below MDL.
*2 (Average of measured concentration of digested sample - average of measured concentration of digested blank) * dilution ratio.
*4 Concentrations of NO_3-N and NO_2-N in the undigested sample - Actual concentration of NO_3-N in the digested sample.

Table 8 Spike recoveries of sample (n=3)

	NO_2-N	**NO_3-N**	**PO_4-P**
Spiked amount (µg/L)	5		
Concentration of unspiked sample (µg/L)	N.D. *1	11.10	N.D.
Concentration of spiked sample (µg/L)	5.29	16.45	5.32
Spike recovery (%) *2	**105.8**	**107.0**	**106.4**

*1 Below MDL.
*2 (concentration of spiked sample – unspiked sample) / spike amount * 100.

■ Conclusion

This application news introduces the analysis of total nitrogen and total phosphorus in environmental water according to standard ASTM D8001. The HIC-ESP was used for measurement in accordance with the standard. Furthermore, stable analysis is possible by using the electro dialysis suppressor ICDS-40A.

<References>

1) ASTM D8001, Standard Test Method for Determination of Total Nitrogen, Total Kjeldahl Nitrogen by Calculation, and Total Phosphorus in Water, Wastewater by Ion Chromatography, ASTM International, West Conshohocken, PA, www.astm.org

01-00593-EN First Edition: Aug. 2023

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