

Determination of Bromate in Drinking and Mineral Water by Isocratic Ion Chromatography with a Hydroxide Eluent

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Introduction

To ensure that the water we drink is safe, it is disinfected. Unfortunately some of the byproducts of disinfection are potentially harmful. Therefore, many countries have established concentration limits for certain disinfection byproducts. Ozonation is an effective disinfection process that is used worldwide, but will produce bromate if the source water contains bromide. Bromate is a potential human carcinogen and its concentration in drinking water is regulated in many countries with the upper limit often set at 10 µg/L — or 3 µg/L in Europe. The introduction to Dionex (now part of Thermo Scientific) Application Note (AN) 167 discusses bromate risk and regulations.¹

Ion chromatography (IC) is an established technique for determining bromate and the disinfection byproducts chlorite and chlorate. Bromate has been determined by IC using either a hydroxide or carbonate eluent and suppressed conductivity detection^{1,2} according to U.S. Environmental Protection Agency (EPA) Method 300.1, Part B.³ The method using a hydroxide eluent is more sensitive than the method using a carbonate eluent, a result of the known advantages of hydroxide eluents for suppressed conductivity detection. Bromate has also been determined using either a hydroxide or carbonate eluent, suppressed conductivity detection, and absorbance detection after either a postcolumn addition of *o*-dianisidine^{4,5} according to U.S. EPA Method 317.0,⁶ or postcolumn reaction to produce the triiodide ion^{7,8} according to Method 326.0.⁹ Methods 317.0 and 326.0 are used for determining bromate concentrations <1 µg/L. All the above IC methods for determining bromate using a hydroxide eluent use gradient elution.

This application update shows that bromate, chlorate, and chlorite can be determined with an isocratic hydroxide eluent to easily meet current bromate regulations. The method was tested with mineral water, a sample that has a higher ionic strength than most drinking water samples and is, therefore, a good test of the method. This method can use either a Reagent-Free™ IC (RFIC™) system or a standard IC system. Unlike the gradient elution method in Dionex (now part of Thermo Scientific) AN 167, this method cannot determine all standard inorganic anions (for example, phosphate).

Equipment

- Thermo Scientific Dionex ICS-1000 Ion Chromatography System*
- To run this as an RFIC application: Thermo Scientific Dionex ICS-2000 Ion Chromatography System
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) Software

*This application can also be executed on other RFIC systems including the Thermo Scientific Dionex ICS-1100 and Thermo Scientific Dionex ICS-5000+ system.

Reagents and Standards

- Deionized water (DI H₂O), 18.2 MΩ-cm resistance or better
- Sodium hydroxide solution, 400 g/L or 50% NaOH
- Stock individual standards of fluoride, chloride, nitrite, bromide, nitrate, and sulfate
- 1000 mg/L each
- Sodium chlorite, 80% (NaClO₂)
- Potassium bromate (KBrO₃)
- Sodium chlorate (NaClO₃)

Preparation of Solutions and Reagents

Stock Standard Solutions

Prepare 1000 mg/L standards of chlorite, bromate, and chlorate by dissolving 0.1676, 0.1308, and 0.1275 g, respectively, in 100 mL DI H₂O.

Mixed Standard Solutions

Appropriate mixed standards are prepared from the 1000 mg/L stock standards. The standard concentration ranges should span the expected analyte concentrations. The concentrations used in this application are shown in Table 1.

Table 1. Concentrations of calibration standards.

Peak Name	Standard 1 ($\mu\text{g/L}$)	Standard 2 ($\mu\text{g/L}$)	Standard 3 ($\mu\text{g/L}$)
Fluoride	500	1,000	2,000
Chlorite	5	10	20
Bromate	5	10	20
Chloride	25,000	50,000	100,000
Nitrite	5	10	20
Chlorate	5	10	20
Bromide	250	500	1,000
Nitrate	250	500	1,000
Sulfate	25,000	50,000	100,000

Eluent Solution

For an RFIC system, the eluent generator produces the eluent using the Thermo Scientific Dionex EluGen™ EGC-KOH cartridge and DI water supplied by the pump. The concentration of eluent is controlled by Chromeleon software.

To prepare a 20 mM sodium hydroxide solution, dilute 4 mL of 400 g/L (10 M) NaOH to 2 L with DI H_2O . When using 50% NaOH, dilute 3.2 g to 2 L with DI H_2O . For more information on preparing hydroxide eluents, please see section 4.5 of the Thermo Scientific Dionex IonPac AS19 column manual (document #065003).

Conditions

Column:	Dionex IonPac AS19 Analytical, 4 × 250 mm Dionex IonPac AG19 Guard, 4 × 50 mm
Eluent:	20 mM KOH (RFIC systems), 20 mM NaOH
Eluent Source:	Dionex EluGen II EGC-KOH cartridge (for RFIC systems)
Temperature:	25 °C
Flow Rate:	1.0 mL/min
Inj. Volume:	200 μL
Detection:	Thermo Scientific™ Dionex™ ASRS™ ULTRA II suppressor, 4 mm, recycle mode
Suppressor Current:	60 mA
Background:	0.9–1.1 μS (RFIC system), 1.5–2.5 μS (prepared eluent)

Results and Discussion

A Dionex IonPac AS19 column set with an isocratic 20 mM hydroxide eluent separates fluoride, chlorite, bromate, chloride, nitrite, chlorate, bromide, nitrate, and sulfate in under 15 min (Figure 1). This separation is possible with either 20 mM KOH prepared by an RFIC system or manually prepared 20 mM NaOH. Chromatograms of the same sample separated with either a prepared eluent or an RFIC eluent differ in total conductivity (not shown). The total conductivity of the 20 mM manually prepared hydroxide eluent is higher than the 20 mM hydroxide eluent generated by the RFIC system. The higher purity of the RFIC eluent yields a lower

Column:	Dionex IonPac AS19 Analytical, 4 × 250 mm Dionex IonPac AG19 Guard, 4 × 50 mm	Peaks:	1. Fluoride 0.3 mg/L 2. Chlorite 1.0 3. Bromate 2.0 4. Chloride 0.6 5. Nitrite 1.5 6. Chlorate 2.5 7. Bromide 2.5 8. Nitrate 2.5 9. Carbonate n.a. 10. Sulfate 3.0
Eluent:	20 mM KOH		
Eluent Source:	Dionex EluGen II EGC-KOH cartridge		
Temperature:	25 °C		
Flow Rate:	1.0 mL/min		
Inj. Volume:	200 μL		
Detection:	Dionex ASRS ULTRA II suppressor, 4 mm, suppressed conductivity, recycle mode		

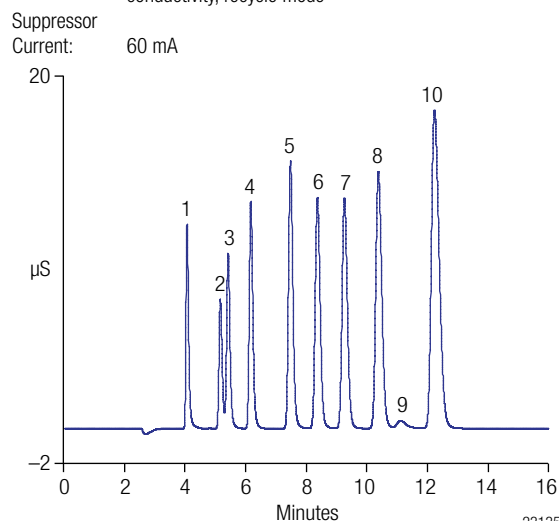


Figure 1. Separation of a mixed anion standard.

background. To determine if this isocratic method is suitable for determining bromate at <10 $\mu\text{g/L}$ together with chlorite and chlorate in a drinking water sample, a standard containing 5 $\mu\text{g/L}$ chlorite, bromate, and chlorate, 25 mg/L chloride and sulfate, and five other anions was prepared. Figure 2 shows a separation of this standard and that the low concentrations of chlorite, bromate, and chlorate are easily detected and resolved from other anions.

Minimum Detection Limit

The minimum detection limit (MDL) for bromate was determined using both manually prepared hydroxide eluent and RFIC eluent by making seven injections of 1 $\mu\text{g/L}$ bromate standard. Figures 3 and 4 show overlays of seven injections for each of the eluent systems, and Tables 2 and 3 show the data from these injections. Using the single-sided Student's t test with a 99% confidence limit, the calculated MDL of bromate with the RFIC system was 0.14 ppb. The calculated MDL for bromate using the IC system with a manually prepared hydroxide eluent was 0.16 ppb. The calculated MDLs are similar, but the baseline of the RFIC system was more stable than the baseline with the manually prepared hydroxide eluent. Consequently, proper peak integration—important for MDL determinations—is easier (that is, requires less postanalysis manipulation of the data to obtain proper integration). A comparison of Figures 3 and 4 reveals the stability of the RFIC system. Both figures were created by overlaying the seven injections with no offset. The injections with the manually prepared hydroxide exhibited variations in the background and baseline, while the injections with the RFIC eluent showed little variation.

Column: Dionex IonPac AS19 Analytical, 4 × 250 mm
Dionex IonPac AG19 Guard, 4 × 50 mm
Eluent: 20 mM KOH
Eluent Source: Dionex EluGen II EGC-KOH cartridge
Temperature: 25 °C
Flow Rate: 1.0 mL/min
Inj. Volume: 200 µL
Detection: Dionex ASRS ULTRA II suppressor, 4 mm, suppressed conductivity, recycle mode

Peaks:

1. Fluoride	0.5 mg/L
2. Unknown	n.a.
3. Chlorite	0.005
4. Bromate	0.005
5. Chloride	25.0
6. Nitrite	0.005
7. Chlorate	0.005
8. Bromide	0.25
9. Nitrate	0.25
10. Carbonate	n.a.
11. Sulfate	25.0

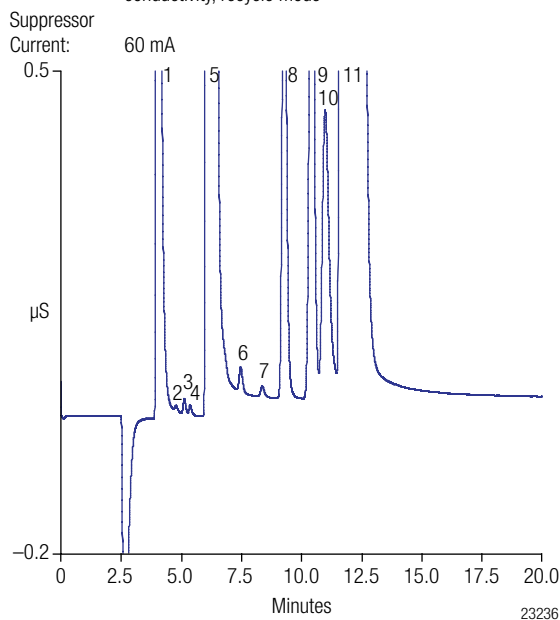


Figure 2. Separation of a mixed anion standard, containing 5 µg/L of chlorite, bromate, and chlorate.

Table 2. Data from the MDL determination of bromate using the RFIC method.

Sample Name	Ret. Time (min)	Area (µS * min x 10 ⁻⁴)
Bromate 1 ppb	5.387	3.21
Bromate 1 ppb	5.397	2.96
Bromate 1 ppb	5.390	3.19
Bromate 1 ppb	5.390	3.40
Bromate 1 ppb	5.393	3.21
Bromate 1 ppb	5.383	3.37
Bromate 1 ppb	5.400	3.22
RSD	0.11%	4.49%

Table 3. Data from the MDL determination of bromate using a manually prepared 20 mM NaOH eluent.

Sample Name	Ret. Time (min)	Area (µS * min x 10 ⁻⁴)
Bromate 1 ppb	5.380	2.83
Bromate 1 ppb	5.383	2.91
Bromate 1 ppb	5.383	3.07
Bromate 1 ppb	5.387	2.83
Bromate 1 ppb	5.367	2.90
Bromate 1 ppb	5.377	2.82
Bromate 1 ppb	5.377	3.23
RSD	0.12%	5.22%

Column: Dionex IonPac AS19 Analytical, 4 × 250 mm
Dionex IonPac AG19 Guard, 4 × 50 mm
Eluent: 20 mM KOH
Eluent Source: Dionex EluGen II EGC-KOH cartridge
Temperature: 25 °C
Flow Rate: 1.0 mL/min
Inj. Volume: 200 µL
Detection: Dionex ASRS ULTRA II suppressor, 4 mm, suppressed conductivity, recycle mode

Suppressor Current: 60 mA

Peaks: 1. Bromate 1 µg/L

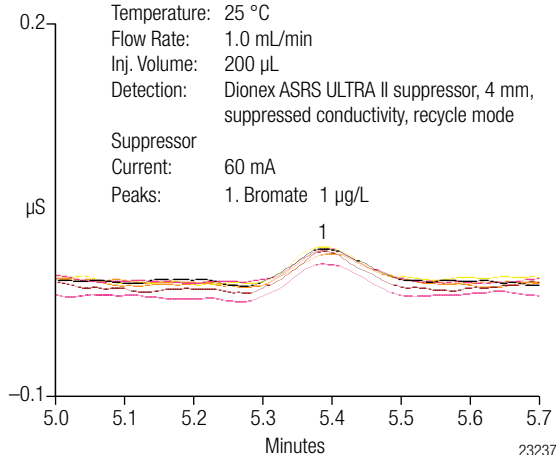


Figure 3. Overlay of seven injections of a 1 µg/L bromate standard with the RFIC method.

Column: Dionex IonPac AS19 Analytical, 4 × 250 mm
Dionex IonPac AG19 Guard, 4 × 50 mm
Eluent: 20 mM NaOH
Temperature: 25 °C
Flow Rate: 1.0 mL/min
Inj. Volume: 200 µL
Detection: Dionex ASRS ULTRA II suppressor, 4 mm, suppressed conductivity, recycle mode

Suppressor Current: 60 mA

Peaks: 1. Bromate 1 µg/L

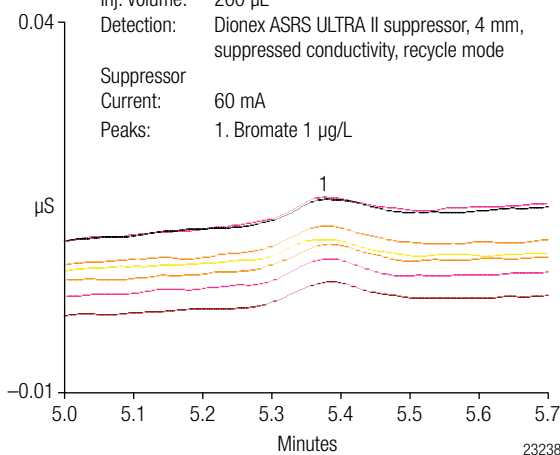


Figure 4. Overlay of seven injections of a 1 µg/L bromate standard with a manually prepared 20 mM NaOH eluent.

Calibration

Standards were prepared at three different concentrations that should be appropriate for mineral and drinking water samples. Figure 2 shows a chromatogram of one of the three standards. The calibration results for both the RFIC eluent and the manually prepared hydroxide eluent are shown in Tables 4 and 5. Each anion exhibited a linear response in its chosen concentration range using either eluent system ($r^2 \times 100 > 99.9$ for all anions). The peaks for the lower analyte concentrations were easier to integrate in the chromatograms run on the RFIC system.

Sample Analysis and Recovery

A bottled mineral water sample was analyzed using either manually prepared hydroxide eluent or hydroxide prepared by eluent generation. Figure 5 shows the separation of the mineral water sample and that no

Table 4. Calibration data for the RFIC eluent.

No .	Ret. Time (min)	Peak	Coeff. Det. (%)	Offset	Slope
1	4.00	Fluoride	99.9913	0.2107	0.0035
2	5.11	Chlorite	99.9963	0.0003	0.0004
3	5.36	Bromate	99.9906	0.0003	0.0003
4	6.19	Chloride	99.9974	1.1322	0.0023
5	7.46	Nitrite	99.9987	-0.0001	0.0011
6	8.35	Chlorate	99.9823	0.0000	0.0006
7	9.27	Bromide	99.9176	-0.0547	0.0010
8	10.41	Nitrate	99.9535	-0.0568	0.0011
9	11.71	Sulfate	99.9988	1.0156	0.0017

Table 5. Calibration data using manually prepared hydroxide eluent.

No.	Ret. Time (min)	Peak	Coeff. Det. (%)	Offset	Slope
1	3.96	Fluoride	99.9710	0.0609	0.0031
2	5.08	Chlorite	99.9937	0.0002	0.0004
3	5.37	Bromate	99.9989	0.0002	0.0003
4	6.17	Chloride	99.9998	0.0314	0.0022
5	7.48	Nitrite	99.9920	-0.0003	0.0010
6	8.46	Chlorate	100.0000	0.0001	0.0005
7	9.34	Bromide	99.9198	-0.0422	0.0008
8	10.55	Nitrate	99.9941	0.0593	0.0011
9	11.98	Sulfate	99.9993	-0.3359	0.0016

chlorite, bromate, or chlorate were detected. To ensure that the 200 μ L of mineral water was not overloading the column, we spiked 10 μ g/L of chlorite, bromate, and chlorate into the mineral water (Figure 6) and evaluated the recovery from five injections of this sample. Tables 6 and 7 show that we observed good analyte recovery using either eluent system with better results using the RFIC system. These results show that the isocratic hydroxide method is suitable for chlorite, bromate, and chlorate determinations in typical drinking and mineral water samples. Using 20 mM hydroxide, phosphate does not elute within 15 min and is probably retained on the column because no broad baseline disturbances were observed in subsequent injections of mineral water. Wash the column with 100 mM hydroxide to prevent the low concentrations of phosphate from lowering column

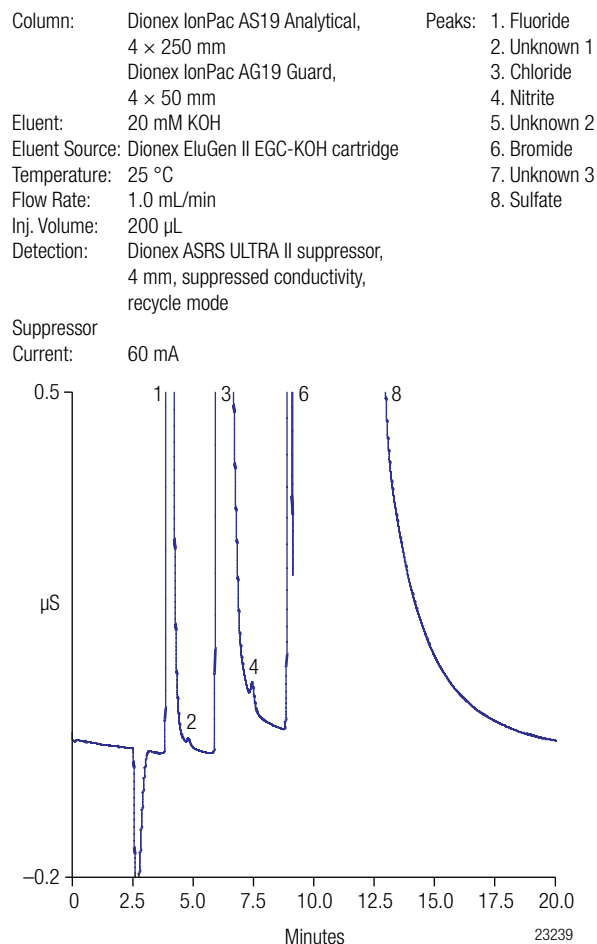


Figure 5. Determination of bromate in a mineral water sample using an RFIC system.

capacity and eventually shortening retention times. Performing the column wash once a week should be adequate because no loss of retention time was observed in two weeks of analysis.

Summary

Bromate was determined in a mineral water sample using the Dionex IonPac AS19 column and isocratic elution. The results of using two sources of eluent, manually prepared hydroxide and hydroxide eluent prepared by an eluent generator, were compared. The results of the MDL, calibration, sample analysis, and percent recovery were used to compare the two eluent sources. The RFIC results were better, but the manually prepared eluents could also determine low μ g/L (<10) levels of bromate in mineral and drinking waters.

Column: Dionex IonPac AS19 Analytical, 4 × 250 mm
 Dionex IonPac AG19 Guard, 4 × 50 mm
 Eluent: 20 mM KOH
 Eluent Source: Dionex EluGen II EGC-KOH cartridge
 Temperature: 25 °C
 Flow Rate: 1.0 mL/min
 Inj. Volume: 200 µL
 Detection: Dionex ASRS ULTRA II suppressor, 4 mm, suppressed conductivity, recycle mode

Peaks:

Peak No.	Compound	Concentration (µg/L)
1.	Fluoride	—
2.	Unknown 1	—
3.	Chlorite	10
4.	Bromate	10
5.	Chloride	—
6.	Nitrite	—
7.	Chlorate	10
8.	Unknown 2	—
9.	Bromide	—
10.	Unknown 3	—
11.	Sulfate	—

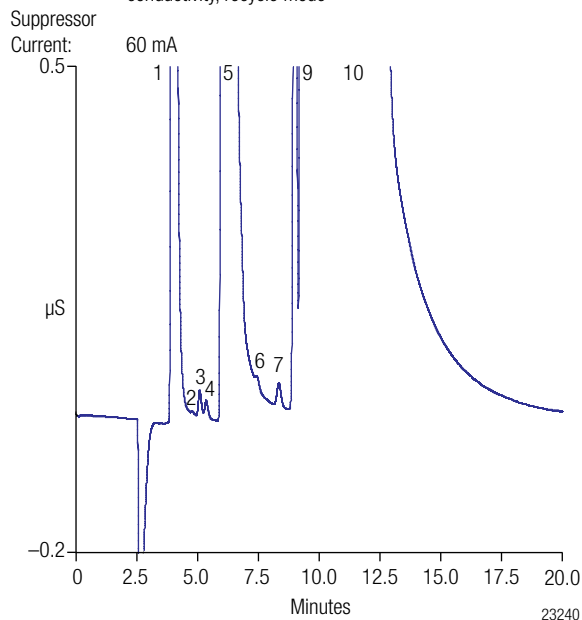


Figure 6. Determination of chlorite, bromate, and chlorate in a mineral water sample using an RFIC system after a 10 µg/L spike of each.

References

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3. U.S. EPA Method 300.1, U.S. Environmental Protection Agency. Cincinnati, OH, 1997.
4. *Determination of Inorganic Oxyhalide Disinfection By-Product Anions and Bromide in Drinking Water Using Ion Chromatography with the Addition of a Postcolumn Reagent for Trace Bromate Analysis.* Application Note 136, LPN 1229-01. Dionex Corporation, (now part of Thermo Scientific) Sunnyvale, CA, 2002.

Table 6. Summary of chlorite, bromate, and chlorate recovery (10 µg/L spike of each) from mineral water with RFIC eluent.

No.	Sample	Amount Chlorite (µg/L)	Amount Bromate (µg/L)	Amount Chlorate (µg/L)
1	Spiked mineral water	10.0338	9.7644	10.5122
2	Spiked mineral water	9.8631	9.5171	10.3528
3	Spiked mineral water	9.9147	9.6518	10.3823
4	Spiked mineral water	9.9843	9.6292	10.4107
5	Spiked mineral water	9.7719	9.6821	10.3929
	Average Amount:	9.9140	9.6490	10.4100
	Recovery (%):	99.14	96.49	104.10

Table 7. Summary of chlorite, bromate, and chlorate recovery (10 µg/L spike of each) from mineral water with manually prepared hydroxide eluent.

No.	Sample	Amount Chlorite (µg/L)	Amount Bromate (µg/L)	Amount Chlorate (µg/L)
1	Spiked mineral water	9.7310	8.9411	11.3125
2	Spiked mineral water	9.8688	8.8031	11.1004
3	Spiked mineral water	9.9669	8.7507	11.1460
4	Spiked mineral water	9.7876	8.7352	11.1813
5	Spiked mineral water	9.7764	8.7353	11.1806
	Average Amount:	9.8260	8.7930	11.1840
	Recovery (%):	98.26	87.93	111.84

5. *Determination of Trace Concentrations of Disinfection By-Product Anions and Bromide in Drinking Water Using Reagent-Free Ion Chromatography Followed by Postcolumn Addition of o-Dianisidine for Trace Bromate Analysis.* Application Note 168, LPN 1706. Dionex Corporation (now part of Thermo Scientific), Sunnyvale, CA, 2005.
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9. U.S. EPA Method 326.0, U.S. Environmental Protection Agency. Cincinnati, OH, 2002.

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