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

INTRODUCTION

To ensure that the water we drink is safe, it is disinfected. Unfortunately some of the by-products of disinfection are potentially harmful. Therefore many countries have established concentration limits for certain disinfection by-products. 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 Application Note 167 discusses bromate risk and regulations.¹

Ion chromatography (IC) is an established technique for determining bromate and the disinfection by-products 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. 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 U.S. EPA 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 Application Note 167, this method cannot determine all standard inorganic anions (e.g., phosphate).

Equipment

ICS-1000 Ion Chromatography System

To run this as an RFIC application:

ICS-2000 Ion Chromatography System

Chromeleon® Chromatography Management Software

*This application can also be executed on other RFIC systems including the ICS-2500 and ICS-3000.

Reagents and Standards

Deionized water (DI H₂O), 18.2 MΩ-cm resistance or better

Sodium hydroxide solution, 400 g/L (Cica-reagent grade, Kantor Chemical) or 50% NaOH (Fisher Scientific)

Stock individual standards of fluoride, chloride, nitrite, bromide, nitrate, and sulfate

1000 mg/L each (Merck)

Sodium chlorite, 80% (NaClO₂, Fluka)

Potassium bromate (KBrO₃, Fluka)

Sodium chlorate (NaClO₃, Fluka)

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 (µg/L)	Standard 2 (µg/L)	Standard 3 (µg/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 EluGen® EGC-KOH cartridge and DI water supplied by the pump. The concentration of eluent is controlled by Chromeleon.

To prepare a 20 mM sodium hydroxide solution, dilute 4 mL of 400 g/L (10 M) NaOH to 2 L with DI H₂O. When using 50% NaOH, dilute 3.2 g to 2 L with DI H₂O. For more information on preparing hydroxide eluents, please see section 4.5 of the IonPac® AS19 manual (document #065003).

CONDITIONS

Column: IonPac AS19 Analytical,
4 × 250 mm (P/N 062885)

IonPac AG19 Guard,
4 × 50 mm (P/N 062887)

Eluent: 20 mM KOH (RFIC systems),
20 mM NaOH

Eluent Source: EluGen II EGC-KOH
(for RFIC systems) (P/N 058900)

Temperature: 25 °C

Flow Rate: 1.0 mL/min

Inj. Volume: 200 µL

Detection: ASRS® ULTRA II, 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

An 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 background. To determine if this isocratic method is suitable for determining bromate at <10 µg/L together

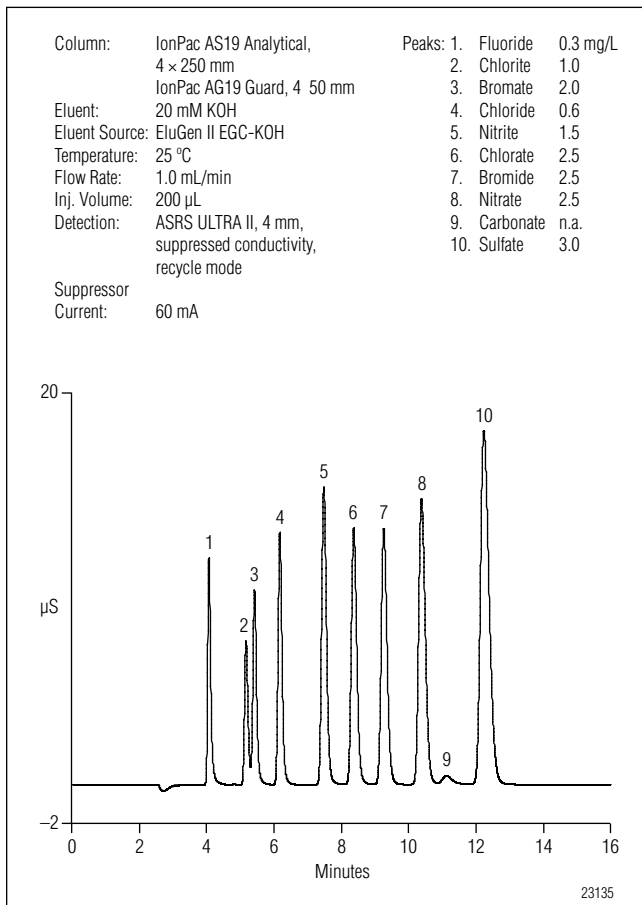


Figure 1. Separation of a mixed anion standard.

with chlorite and chlorate in a drinking water sample, a standard containing 5 µg/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.

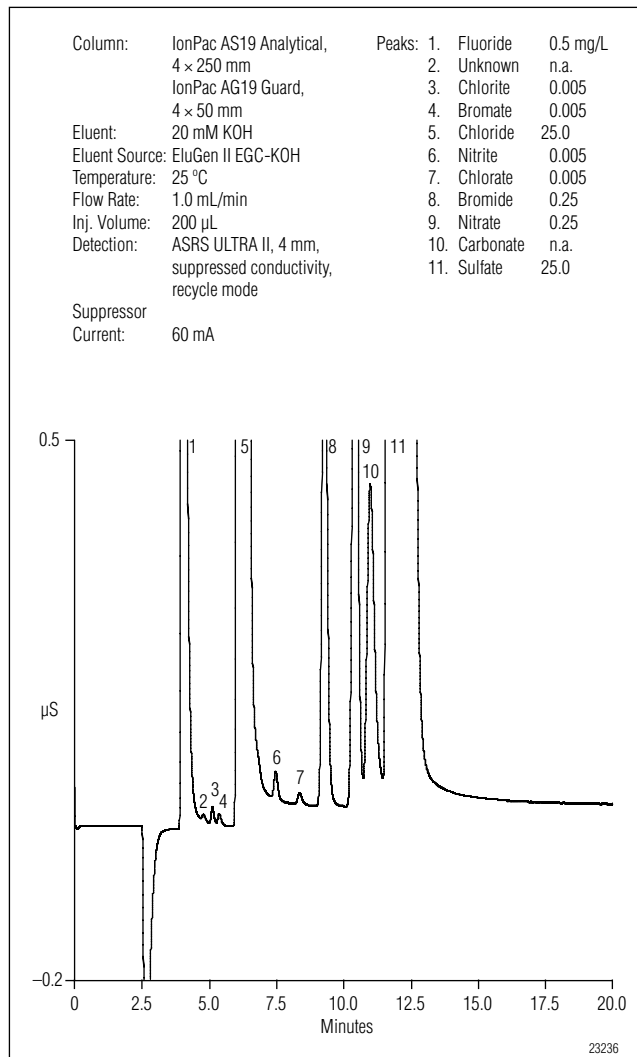


Figure 2. Separation of a mixed anion standard, containing 5 µg/L of chlorite, bromate, and chlorate.

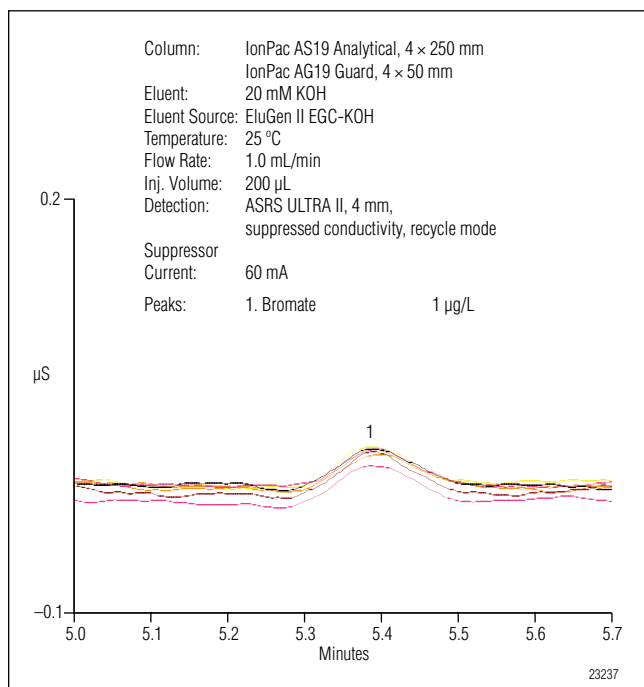


Figure 3. Overlay of seven injections of a 1 µg/L bromate standard with the RFIC method.

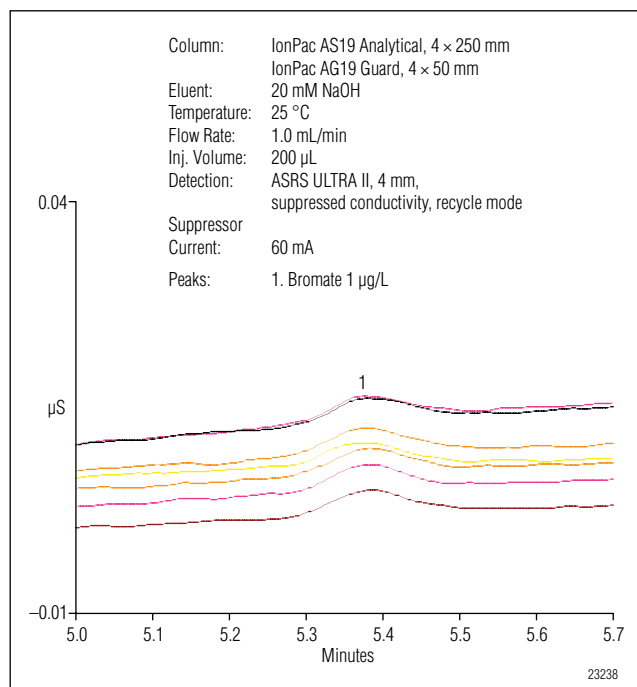


Figure 4. Overlay of seven injections of a 1 µg/L bromate standard with a manually prepared 20 mM NaOH eluent.

Minimum Detection Limit (MDL)

The MDL for bromate was determined using both manually prepared hydroxide eluent and RFIC eluent by making seven injections of 1-µg/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 (i.e., 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.

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.

Table 2. Data from the MDL Determination of Bromate Using the RFIC Method

Sample Name	Ret. Time (min)	Area ($\mu\text{S} * \text{min} \times 10^{-4}$)
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 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 3. Data from the MDL Determination of Bromate Using a Manually Prepared 20 mM NaOH Eluent

Sample Name	Ret. Time (min)	Area ($\mu\text{S} * \text{min} \times 10^{-4}$)
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%

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

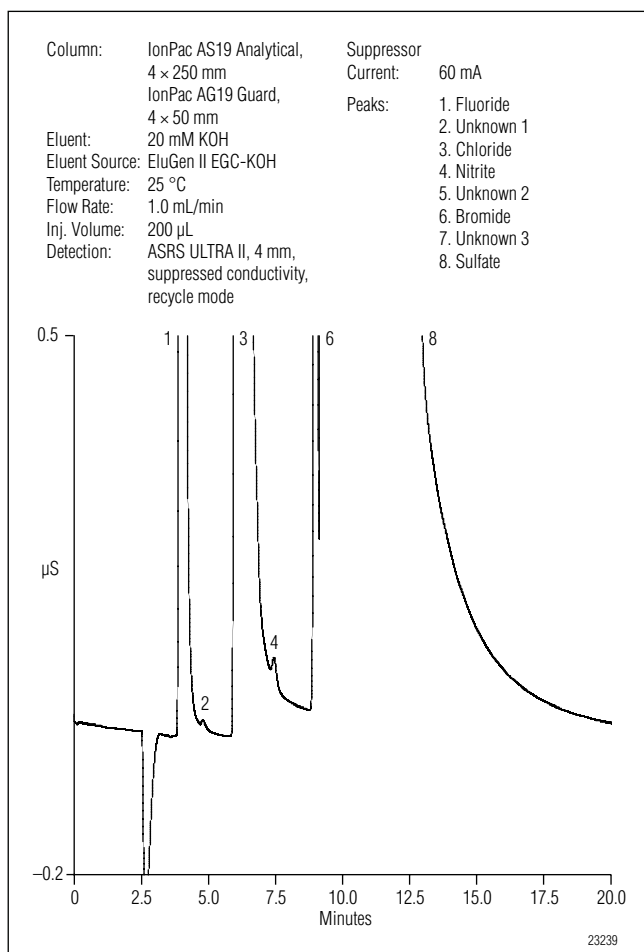


Figure 5. Determination of bromate in a mineral water sample using an RFIC system.

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 chlorite, bromate, or chlorate were detected. To ensure that the 200 µL of mineral water was not overloading the column, we spiked 10 µg/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.

Table 6. Summary of Chlorite, Bromate, and Chlorate Recovery (10 µg/L Spike of Each) from Mineral Water with RFIC Eluent				
Sample 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				
Sample 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

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 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.

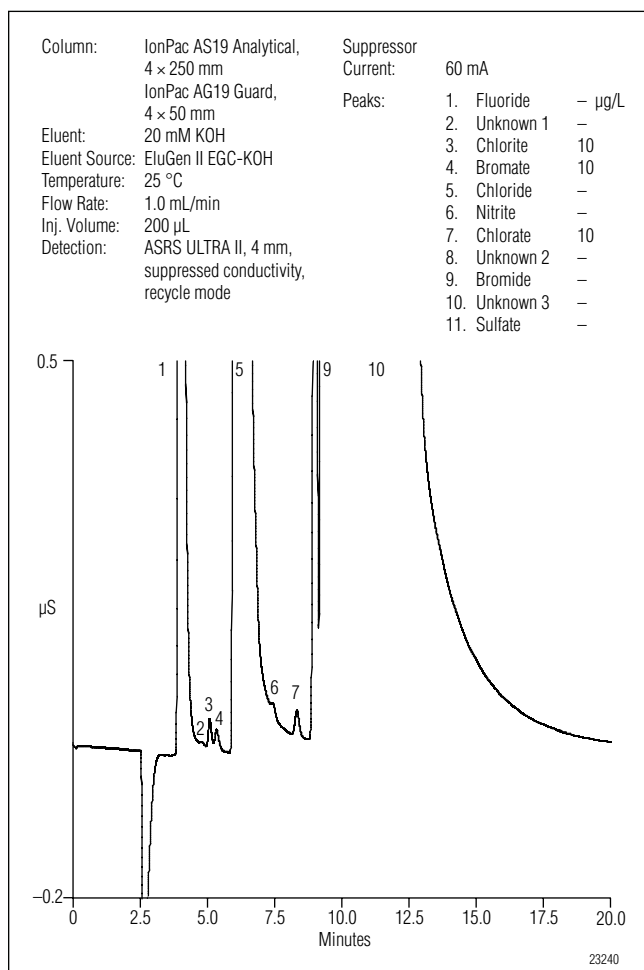


Figure 6. Determination of chlorite, bromate, and chlorate in a mineral water sample using an RFIC system after a 10 µg/L spike of each.

SUMMARY

Bromate was determined in a mineral water sample using the IonPac AS19 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 µg/L (<10) levels of bromate in mineral and drinking waters.

REFERENCES

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8. *Determination of Disinfection By-Product Anions and Bromide in Drinking Water Using a Reagent-Free Ion Chromatography System Followed by Postcolumn Addition of an Acidified On-Line Generated Reagent for Trace Bromate Analysis.* Application Note 171, LPN 1767. Dionex Corporation, Sunnyvale, CA, **2006**.
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SUPPLIERS

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LPN 1793-01 09/06
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