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Energy Dispersive X-ray Fluorescence Spectrometer EDX-7200

Application News

Analysis of Inorganic Elements in Urine Using EDXRF

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User Benefits

- Inorganic elements in urine can be quantified at the ppm level without any complicated sample pretreatment.
- Qual-quantitative analysis is possible using the FP (Fundamental Parameter) method, which does not require standards.
- Qual-quantitative results are obtained within 10 minutes per sample.

■ Introduction

Inorganic element poisoning, including heavy metals, is caused by accidents or criminal incidents, and the causative elements are diverse. Although some of these elements are highly toxic, there are cases in which it is difficult to distinguish them at an early stage because they lack specific symptoms of poisoning. Therefore, analytical methods for rapid screening of these elements are required in forensic research.

Inorganic elements are generally analyzed by ICP-AES or ICP-MS. Although these techniques allow trace-level quantitation, they require chemical pretreatment such as dilution and deproteinization, and the samples are limited to liquid specimens. In contrast, energy dispersive X-ray fluorescence spectrometer (EDXRF) offers sufficient sensitivity in the concentration range associated with poisoning and enables simple, non-destructive analysis in a short time.

This application describes the results of quantitative analysis of 15 elements in urine by the calibration curve method, and qual-quantitative analysis by the FP (Fundamental Parameter) method based on sensitivity coefficients installed in the instrument. The errors in the quantitative values obtained by the FP-based qual-quantitative analysis method were approximately ±20 %, indicating that sufficient quantitative accuracy was achieved. Screening can be performed within 10 minutes per sample.

Fig. 1 EDX-7200

■ Preparation of Calibration Standards

Fifteen elements were selected as the target elements, including those frequently involved in poisoning cases. ICP standard solutions (1000 µg/mL) for each of the fifteen elements were diluted with ultrapure water to prepare standards with element concentrations of 0, 1, 5, 10, 25, and 50 µg/mL. Then, 2.5 mL of each solution was poured into a sample cell with a 5 µm-thick polypropylene film attached to the bottom. Fig. 2 shows the sample image.

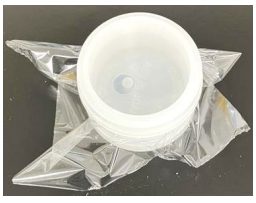

Fig. 2 Sample Image

■ Linearity of the Calibration Curves

Figs. 3 to 5 show the calibration curves. The integration time for the standards was set to 120 s. For matrix correction, internal standard correction using scattered X-rays was applied. In addition, for the quantitative elements listed in Table 1, overlap correction (lj) for coexisting elements was performed. For Ni and Sn, the 1 µg/mL calibration samples were excluded because the sensitivity and measurement time were insufficient.

Table 1 Elements applied with the overlap correction

Quantitative Elements	Overlapping Elements
Cr	V
Cu	Ni
As	Pb
Pb	Se

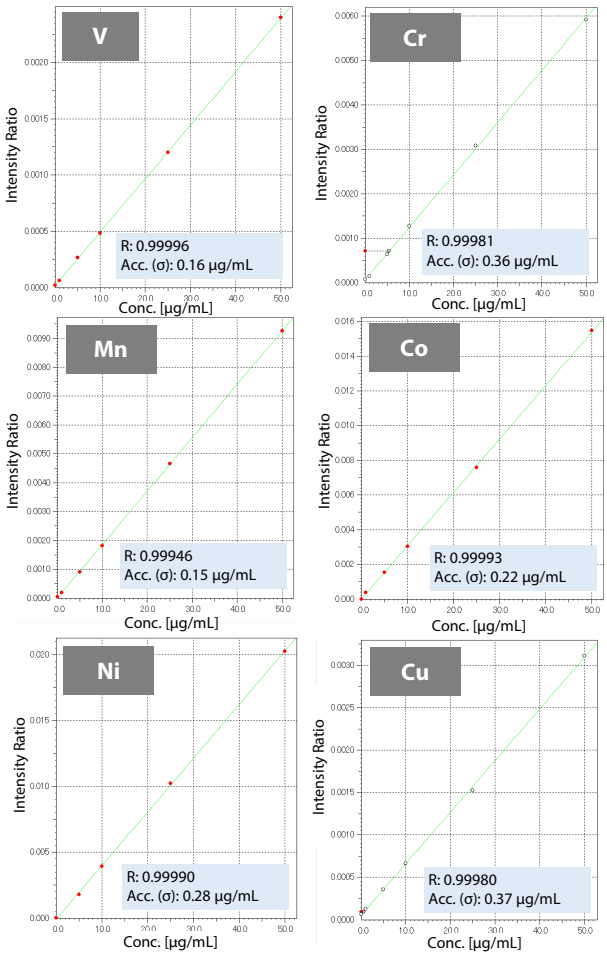

Fig. 3 Calibration Curves Part 1

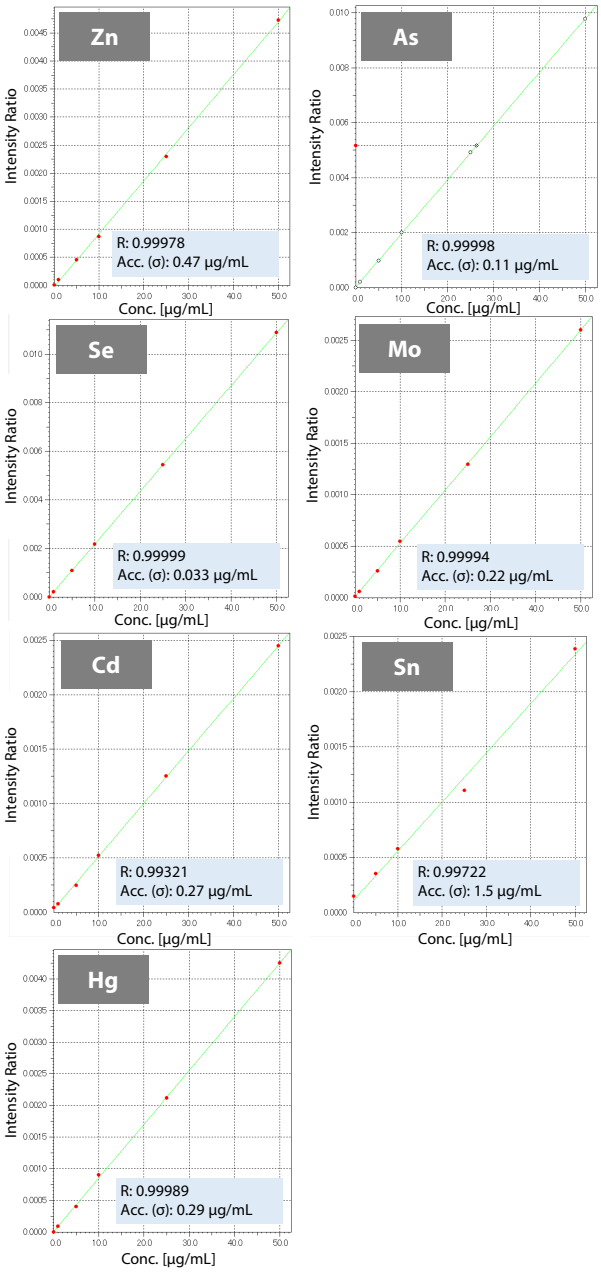

Fig. 4 Calibration Curves Part 2

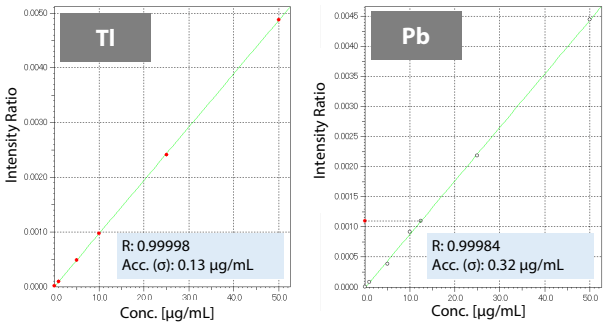

Fig. 5 Calibration Curves Part 3

■ Sample Pretreatment of Urine

To evaluate the quantitative accuracy, human urine purchased from BioIVT was used, and the urine concentration of each element was 10 µg/mL. 0.25 mL of a standard solution (100 µg/mL) was added to 2.25 mL of urine. The mixture was thoroughly mixed using a vortex mixer and then the entire 2.5 mL was poured into a sample cell with a 5 µm-thick polypropylene film attached to the bottom. Fig. 6 shows an image of the samples.

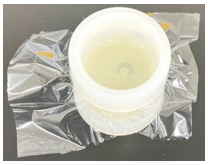

Fig. 6 Sample Image

■ Analysis Results

Fig. 7 shows the qualitative results for urine samples containing 10 µg/mL each of V, Mn, Zn, and Se. In addition, Fig. 8 (next page) shows overlaid profiles of urine samples containing 10 µg/mL of each element and the blank (urine samples before element addition). It was confirmed that the urine samples originally contained elements such as P, S, Cl, K, Ca, Br, and Rb, in addition to the added elements.

Table 2 shows the results of quantitative analysis by the calibration curve method and the qual-quantitative analysis by the FP method. Accuracy ranged from 90 to 111 % for the calibration curve method and from 86 to 124 % for the FP method, indicating that sufficient quantitative accuracy was achieved even with the FP method.

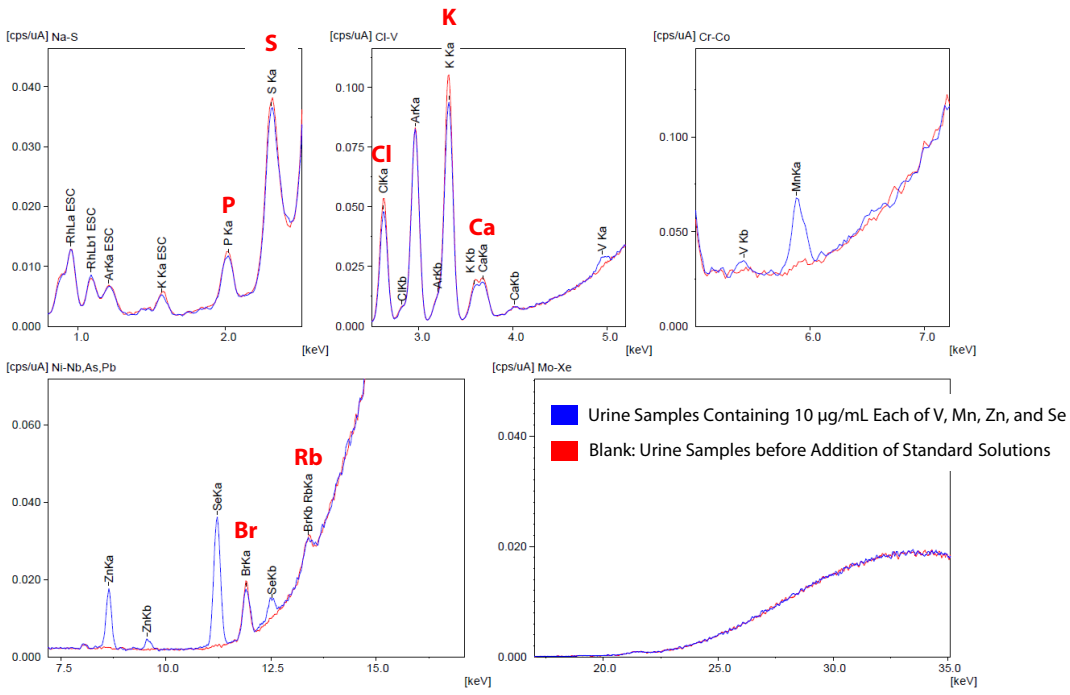

Fig. 7 Qualitative Results (Overlaid Profiles of Urine Samples Containing 10 µg/mL Each of V, Mn, Zn, and Se, and the Blank)

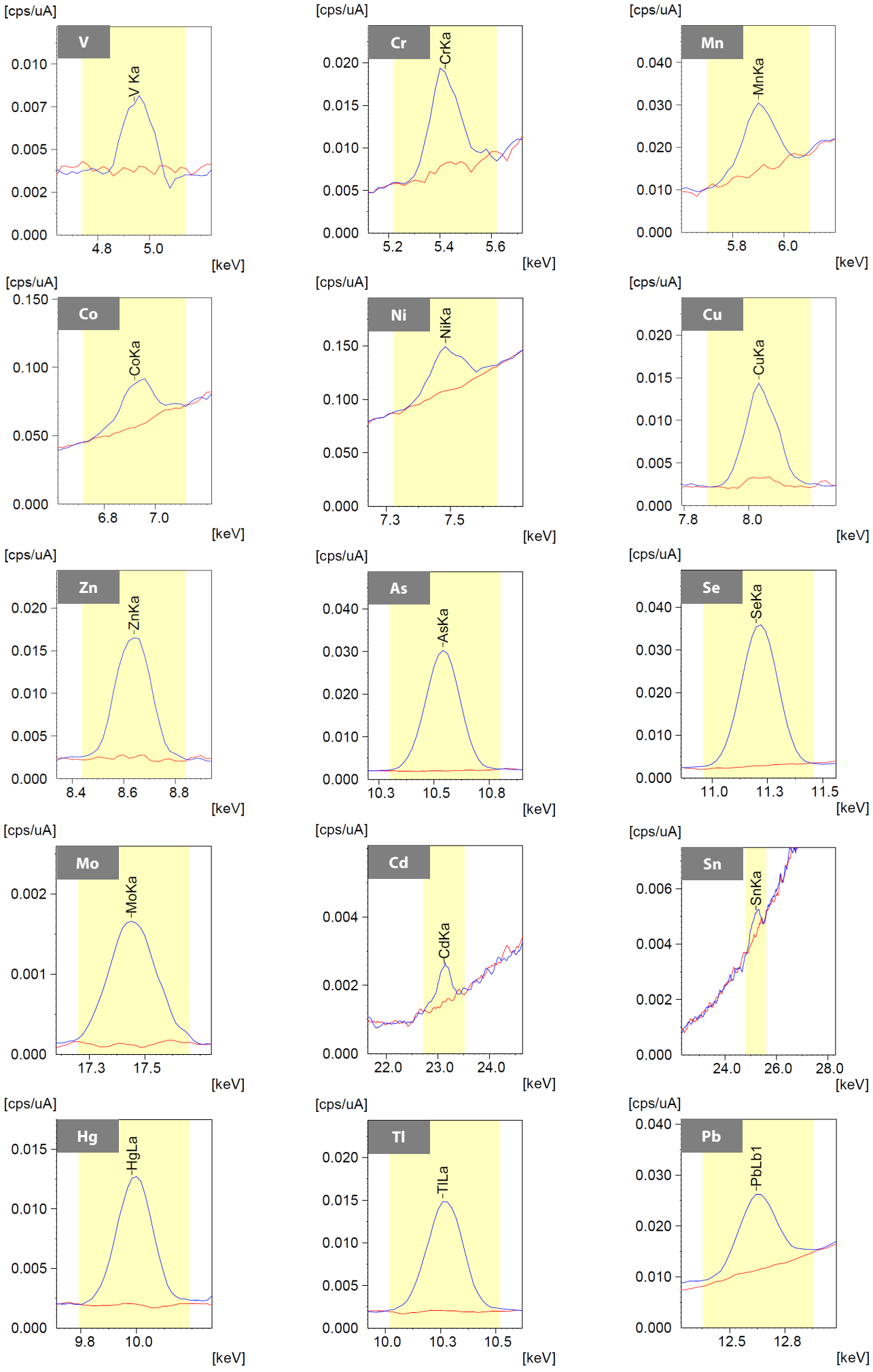

Fig. 8 Overlaid Profiles (Calibration Curve Method, Blue: Each Element 10 µg/mL, Red: 0 µg/mL)

Table 2 Quantitative Analysis Results*1 [μg/mL]

Quant.	$_{23}$V			$_{24}$Cr			$_{25}$Mn			$_{27}$Co			$_{28}$Ni		
	Value	3σ	Accuracy	Value	3σ	Accuracy	Value	3σ	Accuracy	Value	3σ	Accuracy	Value	3σ	Accuracy
Calib.	10.5	2.0	105%	10.2	1.6	102%	10.0	1.2	100%	9.7	1.0	97%	9.2	1.0	92%
FP*2	12.3	2.5	123%	11.9	2.2	119%	9.7	1.5	97%	10.0	1.1	100%	11.9	0.9	119%
Quant.	$_{29}$Cu			$_{30}$Zn			$_{33}$As			$_{34}$Se			$_{42}$Mo		
	Value	3σ	Accuracy	Value	3σ	Accuracy	Value	3σ	Accuracy	Value	3σ	Accuracy	Value	3σ	Accuracy
Calib.	10.1	0.7	101%	9.8	0.5	98%	9.6	0.6	96%	10.2	0.3	102%	10.6	1.0	106%
FP*2	12.4	0.5	124%	12.1	0.5	121%	11.8	0.3	118%	10.3	0.3	103%	9.5	0.8	95%
Quant.	$_{48}$Cd			$_{50}$Sn			$_{80}$Hg			$_{81}$Tl			$_{82}$Pb		
	Value	3σ	Accuracy	Value	3σ	Accuracy	Value	3σ	Accuracy	Value	3σ	Accuracy	Value	3σ	Accuracy
Calib.	10.3	1.7	103%	11.1	3.2	111%	9.0	0.5	90%	9.7	0.5	97%	10.5	0.7	105%
FP*2	9.9	1.7	99%	8.6	2.8	86%	9.8	0.4	98%	10.7	0.4	107%	8.6	0.6	86%

*1 Quant.: Quantitation, Calib.: Calibration Curve Method, FP: Qual-Quantitative FP (Fundamental Parameter) Method, Value: Quantitative Value
*2 In the FP method, moisture and organic components that cannot be measured were treated as H_2O balance (remainder) and quantified.

■ Conclusion

The FP method demonstrated high accuracy for quantitation without calibration curves. Furthermore, urine samples do not require complicated pretreatment such as protein removal, and the analysis time is as short as approximately 10 minutes per sample. This method is well suited for poisoning screening in forensic research.

■ Analysis Conditions

The analysis conditions for the calibration curve method are shown in Table 3, and those for the qual-quantitative analysis using the FP method are shown in Table 4.

Table 3 Analysis Conditions (Calibration Curve Method)

Element	V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sn, Hg, Tl, Pb
Analytical Line	VKα, CrKα, MnKα, CoKα, NiKα, CuKα, ZnKα, AsKα, SeKα, MoKα, CdKα, SnKα,HgLα, TlLα, PbLβ$_1$
Analysis Conditions	Calibration Curve Method (Scattered X-ray Internal Standard Method)
Detector	SDD Detector
X-ray Tube	Rh Target
Tube Voltage	30 kV (V, Cr, Mn, Co, Ni), 50 kV (Cu, Zn, As, Se, Mo, Cd, Sn, Hg, Tl, Pb)
Tube Current	Auto [μA]
Collimator	10 mmφ
Primary Filter	#5 (V), #3 (Cr, Mn, Co, Ni), #4 (Cu, Zn, As, Se, Hg, Tl, Pb), #1 (Mo, Cd, Sn)
Atmosphere	Air
Integration Time*1	60 s × 4 ch (120 s × 4 ch for Calibration Curve Samples Only)
Dead Time	Max. 30 %

*1 An additional 60 s measurement was performed for the internal standard.

Table 4 Analysis Conditions (Qual-Quantitative Analysis)

Element	Na-U
Analytical Line	Kα, Kβ, Lα, Lβ・・・
Analysis Conditions	Qual-Quantitative Analysis (Thin-Film FP Method*1)
Detector	SDD Detector
X-ray Tube	Rh Target
Tube Voltage	15 kV (Na-S), (Cl-V), 50 kV (Cr-Co), (Ni-Nb, As, Pb), (Mo-Xe)
Tube Current	Auto [μA]
Collimator	10 mmφ
Primary Filter	None (Na-S), #2 (Cl-V), #4 (Ni-Nb, As, Pb), #1 (Mo-Xe)
Atmosphere	Air
Integration Time	60 s ×5 ch
Dead Time	Max. 30 %

*1 For a light-element matrix such as urine, the thin-film FP method was applied and the sample thickness was set, taking into account the greater analysis depth for heavy elements.

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