

Speciation of chromium in waste waters by coupled column ion chromatography–inductively coupled plasma mass spectrometry

Mari Pantsar-Kallio*, Pentti K.G. Manninen

Lahti Control and Research Laboratory, Niemenkatu 73 C, FIN-15210, Lahti, Finland

Abstract

An application of coupled column ion chromatography (IC)–inductively coupled plasma mass spectrometry (ICP-MS) is presented for speciation of chromium in waste waters. By coupling an anion column with a cation column, both the cationic Cr(III) and anionic Cr(VI) species can be analyzed with detection limits below 0.5 µg/l. The separation of the interfering ions (chloride, chlorate, perchlorate, sulphate, sulphite, sulphide, thiosulphate, carbonate, cyanide and some organic compounds) from the chromium peaks is discussed, and the use of different chromium isotopes for data acquisition is compared. Based on the results, m/z 52 was considered as an ideal isotope for speciation of chromium in waste waters by the coupled column IC–ICP-MS, because it did not suffer from polyatomic interferences and due to the high sensitivity for chromium. The analysis of the waste water samples should be performed as soon as possible after sampling according to the stability tests of the species.

Keywords: Water analysis; Coupled columns; Chromium; Inorganic ions; Metal cations

1. Introduction

The ability to determine concentrations of Cr(III) and Cr(VI) has become important due to the toxicity of the hexavalent species [1,2] Cr(VI) compounds are found in the environment as a result of industrial pollution, artificial fertilizers, and the use of their compounds as inhibitors.

Conventionally, colorimetric methods have been used in the analysis of hexavalent chromium [3,4]. During the last couple of years, hyphenated techniques have shown their capabilities in speciation analysis and some research groups have developed hyphenated liquid chromatographic methods for speciation of chromium [5–9].

ICP-MS is the most sophisticated analytical method developed for metal analysis; and by using ICP-MS as a multielement detector for chromatographic separation, a very powerful speciation method is obtained. However, like all the other analytical methods, ICP-MS is prone to some interferences when analyzing waste water samples. Probably the most serious interference is the formation of polyatomic ions, especially below atomic mass number 80 [10–12].

Fortunately, the interferences are generally well known: the large concentrations of nitrogen, chlorine, sulphur and carbon may disturb the determination of chromium through formation of ArN^+ , ClO^+ , SO^+ and ArC^+ during analysis [13,14]. Although the relative intensity of the interfering peaks depends on the instrumental and experimental conditions, the total elimination of polyatomic ions is unlikely to be possible when analyzing waste waters

*Corresponding author.

by means of quadrupole instruments and so their effects have to be eliminated in order to get accurate results. In a few laboratories, the interferences have been overcome by using very sophisticated, high resolution ICP-MS [15]. Also, correction formulae based on the isotopic abundances of the interfering matrix element can be used to correct for spectral overlaps [16,17]. Other methods reduce these interferences by electrochemical separation of analytes from matrix [18], gel filtration separation [19] and preconcentration/matrix separation by complexation using bis(carboxymethyl)dithiocarbamate [20]. Although the interfering ions can effectively be separated by HPLC before detection, there are only a few speciation studies for chromium utilizing HPLC-ICP-MS [21–26]. Coupling of ICP-MS as a multielement detector for a chromatographic system also offers lower detection limits than can otherwise be obtained by HPLC.

When analyzing chromium by HPLC-ICP-MS one has to choose the isotopes for data acquisition very carefully by taking the sample type and eluent used into account. Isotopes at m/z 52 and 53 have often been preferred for data acquisition [25,26]. Also m/z 50 has been used in some studies [23,27]. The main focus of this work was to investigate the application of the coupled column IC-ICP-MS method for speciation of chromium in waste water samples and for separation of chloride, chlorate, perchlorate, sulphate, sulphite, sulphide, thiosulphate, carbonate, cyanide and some organic compounds from the chromium species. Also the advantages and disadvantages of using the different isotopes for speciation of chromium in waste waters by coupled column IC-ICP-MS is discussed. Although the waste water samples contain large concentrations of cations also, these do not cause polyatomic interferences for chromium isotopes and do not interfere with the separation of chromium species by coupled column IC-ICP-MS.

2. Experimental

2.1. Ion chromatography

A Pharmacia LKB dual piston reciprocating gradient pump (Model 2249, Pharmacia, Uppsala,

Table 1
The IC gradient programme

Time (min)	Eluent
0.0–2.0	0.4 mM HNO ₃
2.2–3.0	3.2 mM HNO ₃
3.2–6.0	10 mM HNO ₃
6.2–12.0	40 mM HNO ₃

Eluent A was 40 mM HNO₃ and eluent B was water.

Sweden) was used for pumping the eluent. The pump was equipped with a syringe loading sample injector with a loop of 0.5 ml. All the parts in the pump were of metal-free PEEK material. A step gradient with increasing nitric acid concentration and decreasing pH was used for elution. The gradient programme used is presented in Table 1. The anion column (50×4.6 mm, 10 μm) was a Waters IC-Pak A (Waters, Milford, MA, USA) having trimethyl ammonium functionalized groups on polymethacrylate and the cation column was a Waters Guard-Pak CM/D (5×3.9 mm, 5 μm) containing sulphonic acid groups on polybutadiene maleic anhydride silica.

2.2. Inductively coupled plasma mass spectrometry

A Fisons Plasma Quad PQ II+ (VG Elemental, Winsford, UK) with a concentric nebulizer, a Scott-type quartz spray chamber and a Fassel-type quartz torch was used for detection. The data were collected by Time Resolved Analysis (TRA) monitoring the peak heights at m/z 48–60. The instrument sensitivity was optimized daily including optimization of the ion-lens voltages, position of the torch and nebulizer gas flow-rate. The optimized conditions are listed in Table 2.

Table 2
ICP-MS instrumental parameters

Parameter	Value
RF Power (W)	1350
Cool gas flow-rate (l/min)	13.5
Intermediate gas flow-rate (l/min)	0.90
Nebulizer gas flow-rate (l/min)	0.80
Spray chamber temperature (°C)	4
Total acquisition time (s)	720
TRA (m/z)	48–60

2.3. Reagents

The eluent for ion chromatographic separations was supra pure grade nitric acid (Merck, Darmstadt, Germany) diluted with high purity water from the Milli-Q water purification system (Millipore, Milford, USA). The analytical-reagent grade chromium standards — $K_2Cr_2O_4$ and $Cr(NO_3)_3 \cdot 9H_2O$ — like the KCl, $KClO_3$, $KClO_4$, KCN, K_2CO_3 , K_2SO_4 , $NaS \cdot 9H_2O$, Na_2SO_3 and $Na_2S_2O_3 \cdot 5H_2O$ were from Merck. The chromium concentration of $Cr(NO_3)_3 \cdot 9H_2O$ was verified by AAS (Model 1100 B, Perkin-Elmer, Norwalk, USA) by comparing the results with $Cr(NO_3)_3$ standard (Titrisol Merck Art. 9948, Merck).

2.4. Procedures

The columns were purged with water for 4 min between injections; and when they were not in use, 0.1 ml/min of 0.4 mM HNO_3 was pumped through. The air was removed from the eluents by bubbling nitrogen through for 15 min and then keeping the eluent in an ultrasonic bath for 10 min. The standards and samples were filtered through 0.45 μm syringe filters before analysis.

3. Results and discussion

3.1. The coupled column system

Cr(III) and Cr(VI) were analyzed by coupled column IC-ICP-MS; the anion column was coupled on-line with the cation column in order to concentrate both the cationic Cr(III) and anionic Cr(VI) before detection. Retaining both the species in the columns is important in order to ensure that the interfering ions and chromium species do not co-elute in the void volume, which may cause overestimation of the analytes. The schematic diagram of the coupled column IC-ICP-MS system is presented in Fig. 1. Nitric acid gradient from 0.4 mM to 40 mM was used as eluent, giving ideal conditions for ICP-MS detection. The regeneration of the columns was very fast; water was purged through for only 4 min between the injections.

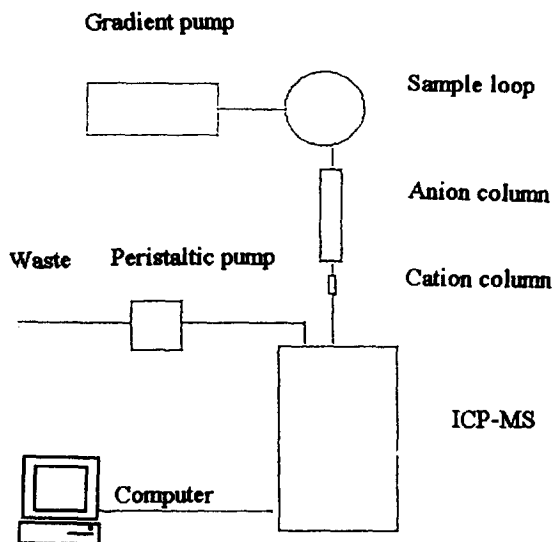


Fig. 1. The schematic diagram of the IC-ICP-MS system used.

3.2. Analysis of waste water samples

Three different kinds of waste waters were analyzed; 1: industrial waste water from a cement industrial process pool, 2: samples from a sewage sludge treatment plant and 3: samples from a wood preservative plant.

3.2.1. The interference of carbon

An ArC^+ peak was detected in the chromatogram at m/z 52 with a carbon concentration larger than about 20 mg/l as HCO_3^- , CN^- or organic carbon in the sample. HCO_3^- , CN^- and most of the organic carbon eluted in the void volume and some of the organic carbon after Cr(III) and thus did not interfere with the speciation of chromium as presented in Figs. 2 and 3. In the chromatogram of waste water 1 (Fig. 2), containing 15 mg/l dissolved organic carbon (DOC) and 44 mg/l dissolved inorganic carbon (DIC), a large ArC^+ peak appeared in the chromatogram (Fig. 2) but did not cause any interferences. The isotope 52 is an ideal one for speciation of chromium in waste waters by coupled column HPLC-ICP-MS because it has a high abundance of chromium and because the interference of ArC^+ could be eliminated.

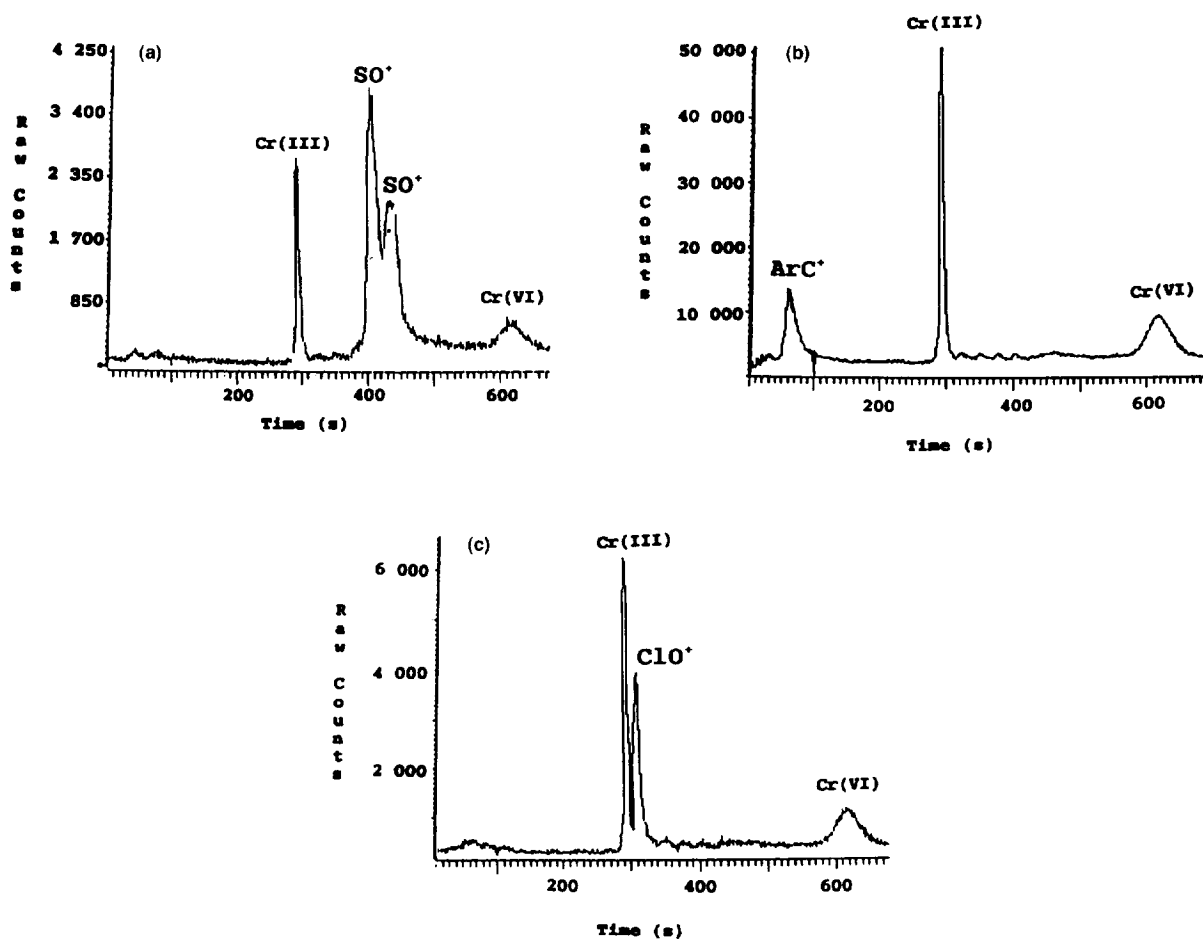


Fig. 2. The chromatogram for waste water 1, for (a) m/z 50, (b) m/z 52 and (c) m/z 53. Cr(III) 10 $\mu\text{g/l}$ and Cr(VI) 8 $\mu\text{g/l}$, DOC 15 mg/l, DIC 44 mg/l, SO_4^{2-} 340 mg/l, Cl^- 34 mg/l. For chromatographic and ICP-MS conditions see Tables 1 and 2.

3.2.2. The interference of chlorine

At m/z 53, the biggest interferences arise from Cl^- in samples — ClO^+ peak height was found to increase almost linearly in the range of 10–1000 mg/l Cl^- . The interference of Cl^- was eliminated at m/z 53, as Cl^- eluted after Cr(III) (Fig. 2) and even an increase in Cl^- concentration from 10 mg/l to 100 mg/l did not affect the peak height of Cr(III). If a sample contains larger Cl^- concentrations than 100 mg/l, dilution or using m/z 52 for data acquisition is necessary, because the ClO^+ peak was not fully separated from Cr(III). Even 100 mg/l of ClO_3^- or ClO_4^- in the sample did not produce any inter-

ferences, as ClO_3^- eluted between Cr(III) and Cr(VI), and ClO_4^- eluted after Cr(VI).

3.2.3. The interference of sulphur

Sulphur (as SO_4^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$ or S^{2-}) in concentrations larger than 3 mg/l caused interferences in the chromatogram as SO^+ at m/z 50. The separation of SO_4^{2-} and $\text{S}_2\text{O}_3^{2-}$ from the chromium species is presented in Figs. 2 and 3. The SO^+ peak increased linearly in a range of 5–1000 mg/l SO_4^{2-} . S^{2-} did not interfere with the analysis, as it eluted in the void volume. The most serious interference arose from SO_3^{2-} in the sample, as it co-eluted with

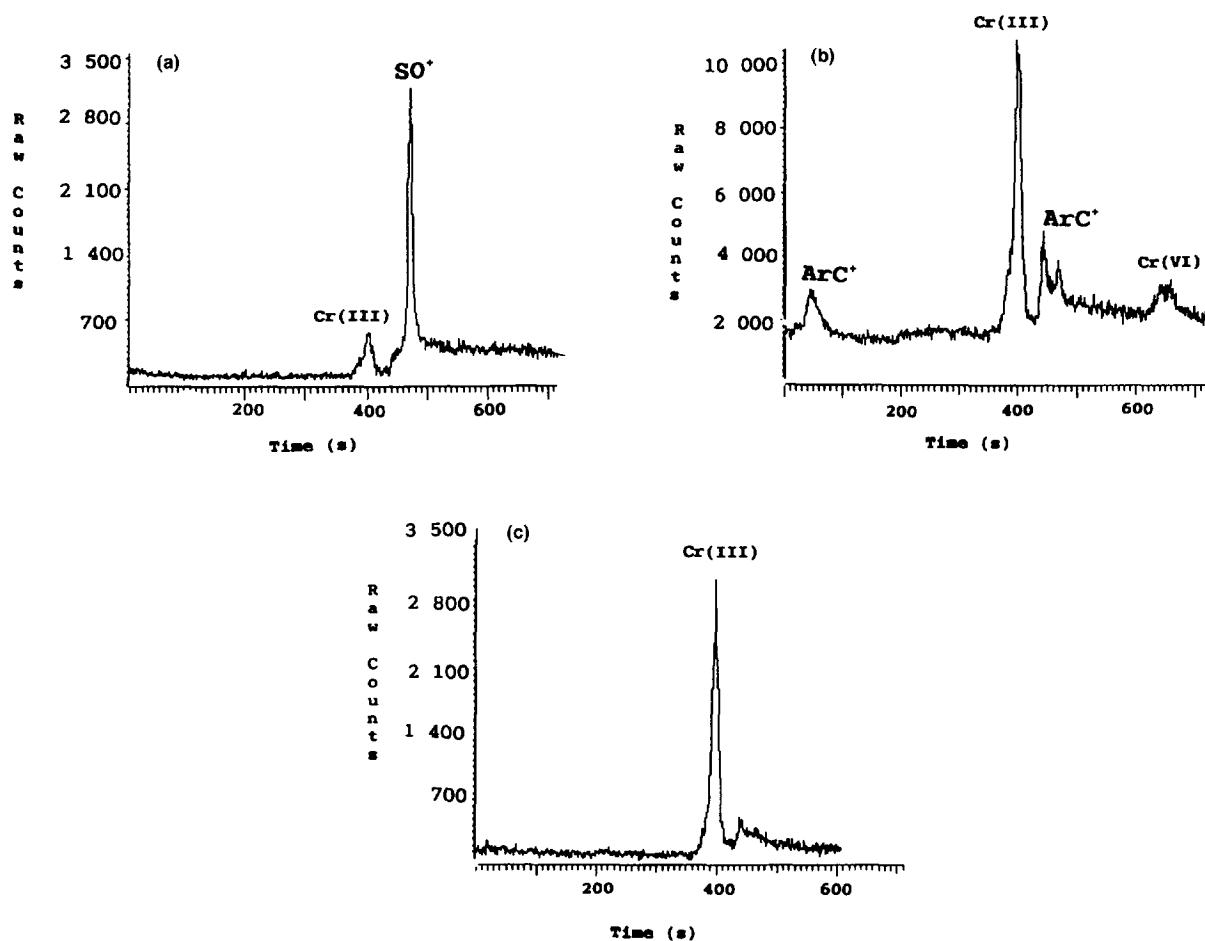


Fig. 3. The chromatogram for waste water 2, for (a) m/z 50, (b) m/z 52 and (c) m/z 53. Cr(III) 2 $\mu\text{g/l}$ and Cr(VI) 1 $\mu\text{g/l}$, DOC 27 mg/l, DIC 15 mg/l, SO_4^{2-} 180 mg/l, Cl^- 13 mg/l. For chromatographic and ICP-MS conditions see Tables 1 and 2.

Cr(III), preventing its direct analysis at m/z 50. If m/z 50 is, anyway, used in the analysis of Cr(III), then also m/z 48 should be monitored in order to check the concentration of SO^+ . However, due to the low abundance of chromium at m/z 50, isotopes 52 or 53 are mostly preferred.

3.3. The linearities, detection limits and repeatabilities

The figures of merit are presented in Table 3. The regression analysis was performed to test the linearity for the peak heights of the waste water sample

spiked with 1, 3, 9, 30, 90 and 250 $\mu\text{g/l}$ Cr(III) and Cr(VI) ($n=3$, except for 250 $\mu\text{g/l}$ $n=1$). The large concentrations of different compounds in the sample did not affect the detection limits of the chromium species by coupled column IC-ICP-MS. The detection limits at m/z 52 for waste water samples were 0.3 $\mu\text{g/l}$ for Cr(III) and 0.5 $\mu\text{g/l}$ for Cr(VI), determined as three times the standard deviation of the blank. At m/z 53, the detection limits were 2 $\mu\text{g/l}$ for Cr(III) and 2 $\mu\text{g/l}$ for Cr(VI); and at m/z 50, 2 $\mu\text{g/l}$ for Cr(III) and 5 $\mu\text{g/l}$ for Cr(VI). The better detection limit for Cr(III), compared with Cr(VI) was due to the better peak shape. The m/z 54

Table 3

The merit of figures for peak heights of Cr(III) and Cr(VI) at *m/z* 50, 52 and 53

	Cr(III)			Cr(VI)		
	<i>m/z</i> 50	<i>m/z</i> 52	<i>m/z</i> 53	<i>m/z</i> 50	<i>m/z</i> 52	<i>m/z</i> 53
R^2 ^a	0.9999	0.9997	0.9998	0.9986	0.9989	0.9999
Slope ^a	262	6392	704	37	808	85
DL ($\mu\text{g/l}$) ^b	2	0.3	2	5	0.5	2

For chromatographic and ICP-MS conditions see Tables 1 and 2.

^a Regression was calculated for industrial waste water spiked with 1, 3, 9, 30, 90 and 250 $\mu\text{g/l}$ Cr(III) and Cr(VI).^b Detection limit defined by 3 times the standard deviation of the blank.

cannot be used for analysis of chromium, because of the high ArN^+ signal arising from the nitric acid eluent.

The repeatabilities were tested for waste water sample 1 ($n=10$) at isotope 52, which was found to be the best isotope for speciation of chromium in waste waters by coupled column IC-ICP-MS. The repeatability was very good, with RSD=2.3% for Cr(III) and RSD=1.2% for Cr(VI).

3.4. The stability of the species

The stability tests showed the importance of analyzing the waste water samples as soon as possible after sampling. Even though the chromatographic system used can give high accuracy, the results can be quite misleading due to losses of the species by species conversion, complexation, sorption and reduction/oxidation during storage. All these phenomena depend greatly upon the sample type and are thus quite different for various kinds of waters [28]. For example, in samples with high TOC concentration the recoveries of the chromium species are usually low, because Cr(VI) oxidizes and Cr(III) adsorbs and complexes with the organic matter.

The stability of the chromium species in the industrial waste water sample, pH=7.9, was studied by keeping the sample containing 3.4 $\mu\text{g/l}$ Cr(III) and 2.6 $\mu\text{g/l}$ Cr(VI) in a refrigerator (+4°C) for 320 h. The stability diagram is presented in Fig. 4. The explanation for the losses was assumed to be species conversion and complexation/sorption of the species in the unfiltered sample.

The stability of the species was also studied for 60 h in a standard solution containing 8 mg/l TOC and 10 $\mu\text{g/l}$ Cr(III) and Cr(VI) at pH 5 and 8. At pH 5 the stability of Cr(III) was good with recovery of

94% after 60 h, while the recovery for Cr(VI) was less than 10%. At pH 8, correspondingly after 60 h, the recovery for Cr(VI) was from 93 to 130%, while the recovery for Cr(III) was only from 0 to 24%. These results indicate pH dependent species losses due to adsorption, complexation and species conversion.

4. Conclusions

This study presents a speciation method for chromium in waste water samples by coupled column IC-ICP-MS. With the system developed, the simultaneous chromatographic determination of the cationic and the anionic species is possible. The method is also capable of eliminating the disturbing effects of interfering compounds and elements in speciation analysis of chromium. Quite low concentrations such as 20 mg/l of carbon, 10 mg/l of

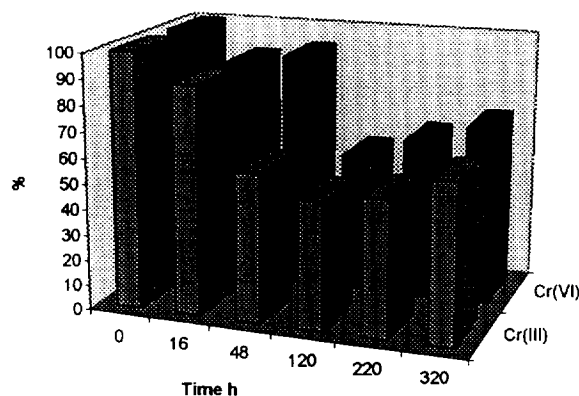


Fig. 4. The stability of the chromium species in the industrial waste water sample, pH 7.9, containing 3.4 $\mu\text{g/l}$ Cr(III) and 2.6 mg/l Cr(VI).

chlorine and even 3 mg/l of sulphur can cause overestimation of chromium if not properly resolved. The stability tests showed the importance of analyzing the samples as soon as possible after sampling.

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