

Determination of Trace Elements in River Arakawa

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The river stems from a mountain, runs through the land and flows in the sea. She covers the area of the mountain side, that of the agricultural field and that of the city which is crowded by the people. The function is important for the sustenance of the good life of people of good quality, because the river water in the country side area works as the source of the ground water which is used in the daily life, and works in the agricultural field as that of the irrigation water for the rice and vegetables. Moreover, in the modern days, the river has a key function in the city life as the source of tap water.

Accordingly, the data on the quality of the river water are the controls of great importance for the human activities of modern days.

How we can meet this condition of the river? We should recognize the river as a system of information, where creation of information (data production), data accumulation, then networking of those data must be formulated as a system. For data creation, experimental science must work. For systematization of the data, information scientists should join and work.

Top level work in the experimental science is needed for data creation. Patient and enormous efforts are also necessary for accumulation of the data. This report will call the attention of the information scientists for the fact that the subject of the experimental science needs the eyes of information scientists.

Human lives of modern time hold the danger of having hazardous chemical substances in water which needs chronological monitoring. But, first of all, the methods of measurement of those substances with the highest sensitivity and accuracy must be invented, and then this method must be applied in reality. This paper will report the results of the invention of the method and application of the said method for six monitoring sites of the river.

As a matter of the future problem, the on-line base data access and the networking of those monitoring stations must be materialized, although some experimental stations are already being built in this country. This paper will be presented as an example which refers to the importance of the eyes to see the river as an information system which bridges multiphases of the modern lives.

Keywords: river water, trace elements, arsenic, selenium, antimony, tin, hydride generation, atomic absorption spectrometry

1. Introduction

River Arakawa flows from the east slope of Mount Kobushi 2,475 m high, flows through Saitama District and flows into The Tokyo

Bay. The main stream of River Arakawa is 169 km long. River Arakawa has 120 branch streams. The total length of River Arakawa including all branch streams is 1,187 km. About eight hundred million people live in the basin of River Arakawa. At Ochiai, the River joins with River Nakatsu. There was Chichibu Mine at the source of River Nakatsu. Chichibu Mine produced several minerals, such as gold, silver, copper, lead, zinc, manganese and nickel, but the minerals are now exhausted. Figure 1 shows a map of River Arakawa.

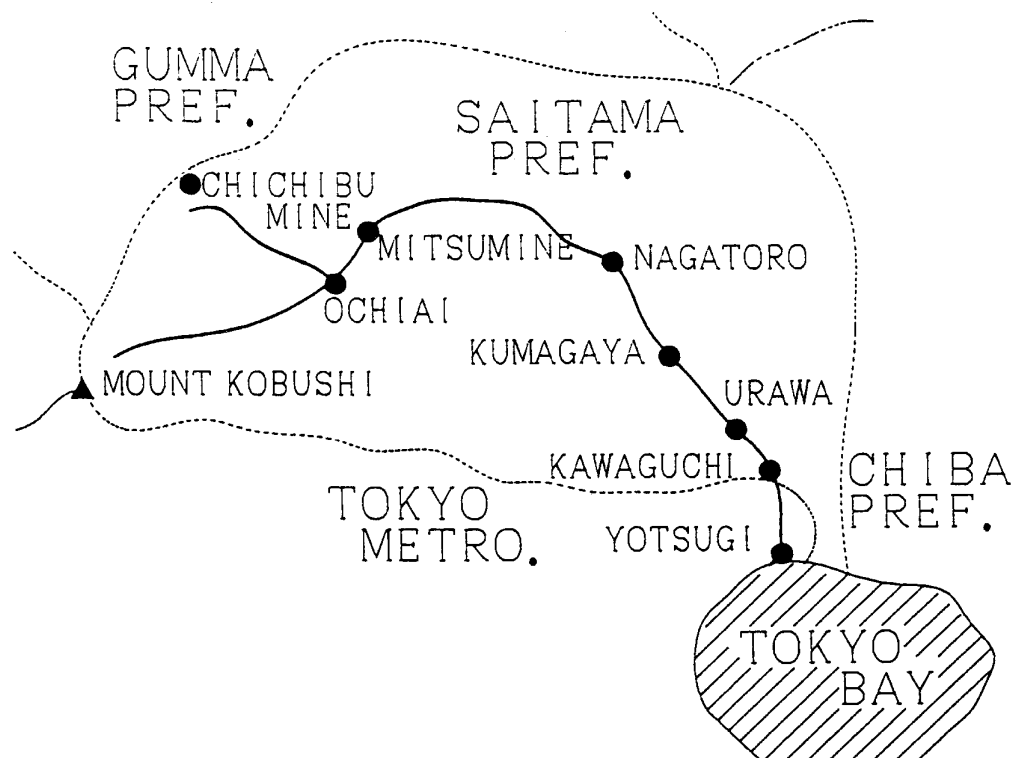


Figure 1. A map of River Arakawa.

Several chemical components in River Arakawa have been analyzed routinely by Ministry of Construction and some public institutions in Saitama Prefecture. A high sensitive method for determining hydride forming elements was found by Schmidt and Royer in 1973(1). They used sodium borohydride as a reductant of arsenic, selenium, antimony and bismuth. The author have assembled an automated hydride generation apparatus and determined trace elements, especially hydride-forming elements, such as arsenic, selenium, antimony and tin, in River Arakawa as a practical sample collected at several sites by hydride generation atomic absorption spectrometry.

In Japan, Standards for city water quality was revised in December, 1992 by Ministry of Public Welfare, and the new Standards was then executed in December, 1993. In this Standards, arsenic and selenium contents in city water are regulated to be less than 10 ppb for human health. Antimony content should be watched to be less than 2 ppb. Iron and copper are regulated to be less than 300 ppb and 1,000 ppb,

respectively, to keep the quality of city water.

2. Experimental

2.1 Apparatus and Instrumentation

A Nippon Jarrell-Ash AA-782 atomic absorption spectrometer equipped with Hamamatsu Photonics hollow cathode lamps was used for atomic absorption spectrometry under the following operating conditions: wavelength, arsenic 193.7, selenium 196.0, antimony 217.6 and tin 224.6 nm; lamp current, arsenic 10, selenium 20, antimony 10 and tin 20 mA. The signals were recorded on a Yanagimoto YR-110 chart recorder at a chart speed of 4 cm/min with a scale expansion of 3 times, and a damping of 0.2 s.

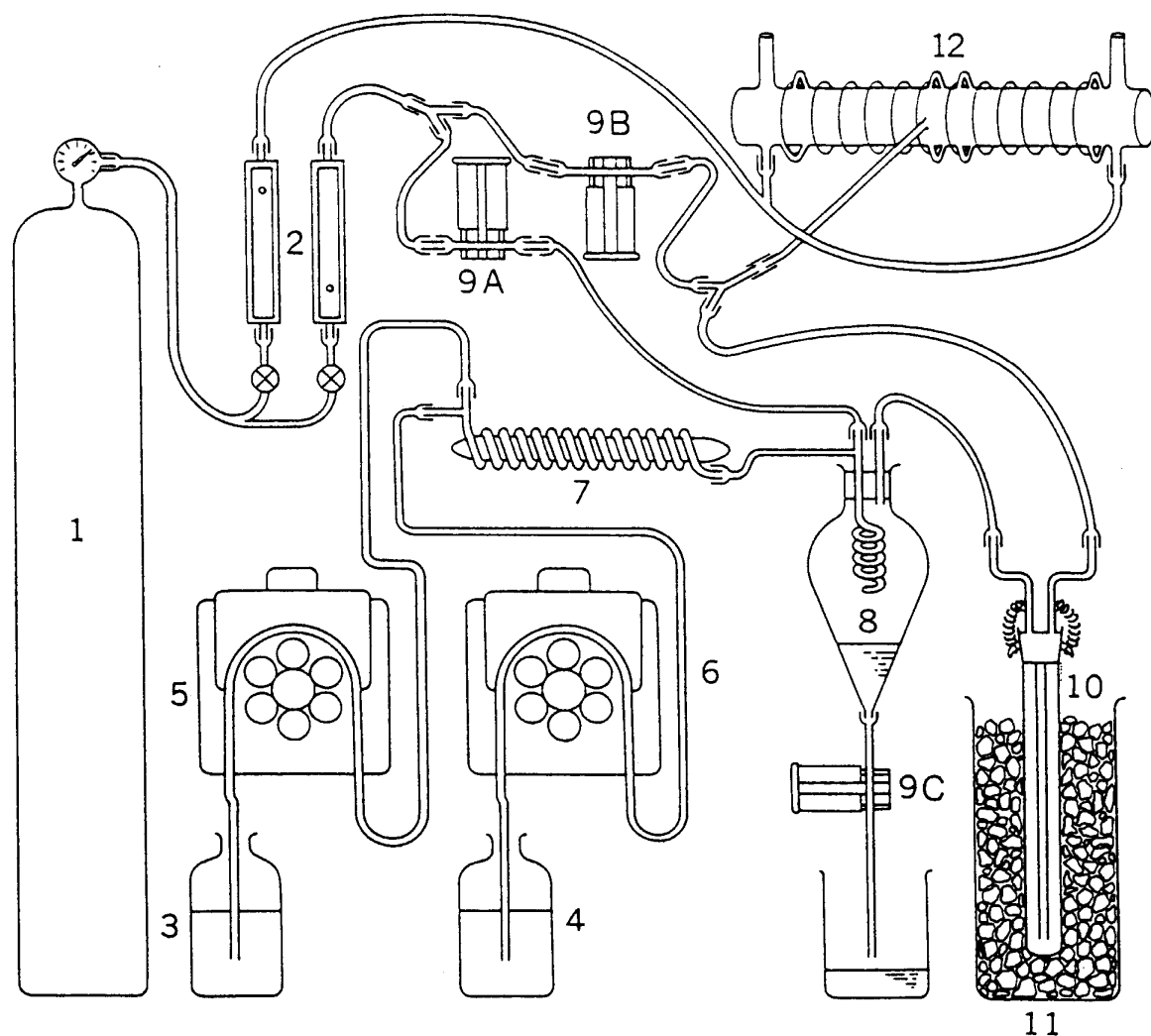


Figure 2. Schematic diagram of the hydride generation system for determining arsenic and selenium. 1, nitrogen gas cylinder; 2, flow meters; 3, sample solution container; 4, sodium borohydride solution container; 5, 6, peristaltic pumps for sample solution and sodium borohydride solution; 7, Pyrex glass mixing coil; 8, 50-ml Pyrex glass gas-liquid separator; 9A, 9B and 9C, electromagnetic solenoid pinch valves; 10, water vapor trap; 11, ice bath; 12, electrically heated quartz furnace.

Figure 2 illustrates the hydride generation system for the determination of arsenic and selenium. Two variable speed peristaltic pumps (SJ-1211H, Atto, Tokyo, Japan) were fitted with Tygon tube (R-3603, 3.96 mm o.d., 2.38 mm i.d.) to the Pyrex mixing coil (2 mm i.d., 16 cm long). The 50-ml Pyrex gas-liquid separator contained a spiral tube to exhaust the gas efficiently. A glass trap (15 mm i.d., 21 cm long) immersed in an ice bath was used to remove water vapor in the hydride gas. Silicone tubes (Shin-etsu Polymer, Tokyo, Japan) 5 mm o.d., 10 cm long were pinched with electromagnetic solenoid pinch valves (Pinch Valve PK-305-NO, 13 W, Takasago Electric Industries, Nagoya, Japan) in order to control the gas flow. An open-ended atomic absorption cell, 12, was constructed from a quartz tube furnace 18 mm o.d., 23 cm long. Each half length of the quartz tube was wound 35 times with 0.5-mm Kanthal alloy wire holding an asbsetos string between the wire windings and then wrapped triply with a quartz tape of 3 cm width. The tube furnace was clamped with porcelain segments and its axis was aligned into the optical axis of the spectrometer and heated to 900 °C.

When antimony and tin are determined, the water vapor trap, 10, and the ice bath, 11, in Figure 2 are eliminated, since no light absorption with water vapor is observed for antimony and tin.

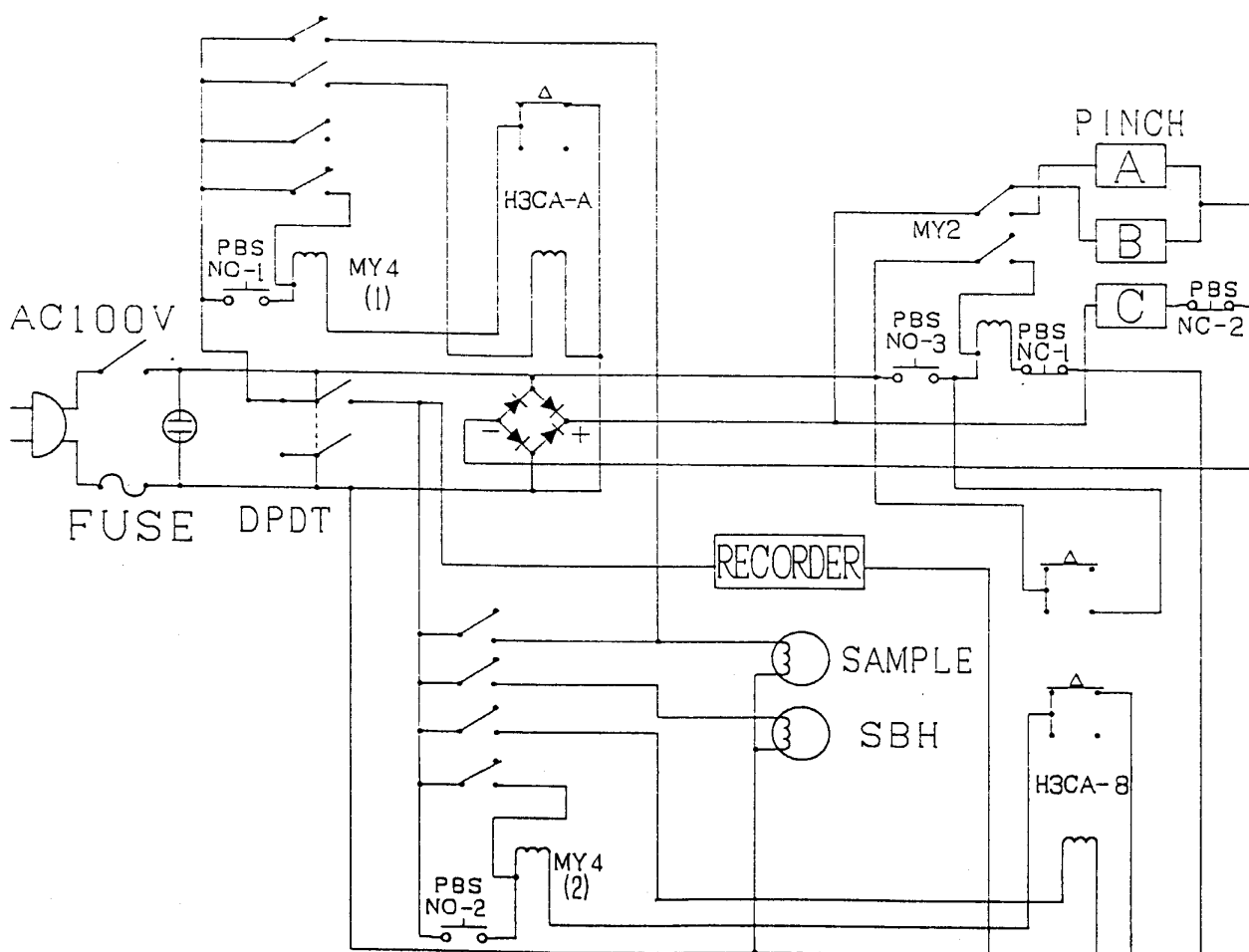


Figure 3. Electrical circuit diagram for the hydride generation system.

Figure 3 shows the electrical circuit diagram of the system. The circuit consists of one double pole and two quadruple pole electromagnetic relays (MY2 and MY4, OMRON, Osaka, Japan) and two OMRON solid-state timers, H3CA-A (operation mode A) and H3CA-8. The H3CA-A has a single pole double throw (SPDT) contact, while the H3CA-8 timer has a double pole double throw (DPDT) contact. The solenoid pinch valves were operated with direct current which was supplied by rectifying commercial alternating current (100 V) with a silicon rectifier (5B3, International Rectifier, El Segundo, CA).

The circuit was manipulated by pressing the push-button switches (PBS) of the normally opened (NO) and normally closed (NC) types. The relays were self-retained by pressing PBS NO-1 and NO-2, and were released automatically with H3CA-A and H3CA-8 timers, respectively. The solution of waste in the separator was drained by pressing the PBS NC-2. A double pole double throw (DPDT) switch (DS-015, Miyama Electric Parts, Tokyo, Japan) was used to switch from the sample injection mode to the mixing mode.

Iron and copper were determined with a Hirma 6 spectrophotometer. They were determined with 1,10-phenanthroline(7) and neocuproine(8), using filters of 517 and 460 nm for iron and copper, respectively.

2.2 Pretreatment of river water(4)

The water was acidified with 3 ml of concentrated nitric acid, 1 ml of 9 M sulfuric acid and 1 ml of 60% perchloric acid in a Kjeldahl flask containing boiling chips. The digests including siliceous residues were transferred into a 50-ml platinum dish with water. The residues were dissolved with 1 ml of 46% hydrofluoric acid. After the addition of 1 ml of 9 M sulfuric acid, the contents were again evaporated to approximately 2 ml and transferred into a 50-ml beaker.

The pH of the solution was adjusted to 3.5 in the beaker with 1 M ammonia solution. The solution was passed to a column loaded with Chelex 100 at a flow-rate of 1 ml/min. The column was washed twice with 10-ml aliquots of water. The solution was used for each determination. Special notice for each element is given below.

2.3 Arsenic(2,4)

There is a difference of reduction efficiency with sodium borohydride between arsenate and arsenite. However, the arsenic contents were determined as arsenate, since all the arsenic in the sample water was oxidized to arsenate.

2.4 Selenium(2,4)

Since selenate does not form hydrogen selenide with sodium borohydride, selenate is reduced to selenite by heating with concentrated hydrochloric acid.

2.5 Antimony(3)

Since antimony would be complexed with chloride ion, the pretreated sample solution was acidified with sulfuric acid. Potassium iodide solution was added just before measurement to

Table 1. Analytical results of trace elements (ppb) in River Arakawa(2-6)

Site	As	Se	Sb	Sn	Fe	Cu
Mitsumine	3.3-3.8	0.34-0.37	0.42-0.42	0	12-20	4.5-5.5
Nagatoro	1.5-1.7	0.26-0.32	0.16-0.18	0.05-0.07	20-27	1.1-1.5
Kumagaya	1.2-1.5	0.11-0.14	0.18-0.20	0.26-0.41	12-89	3.4-3.4
Urawa	1.0-1.2	0.12-0.13	0.27-0.31	0.26-0.41	134-263	1.2-2.0
Kawaguchi	1.8-1.9	0.42-0.48	0.31-0.39	0.38-0.55	--	--
Yotsugi	3.6-4.0	0.15-0.17	0.91-0.93	--	--	--

Table 2. Chronological change of arsenic and selenium (ppb) in River Arakawa(2,4,6)

Site	As		Se	
	1983	1987	1983	1987
Mitsumine	3.5	3.3-3.8	0.11	0.34-0.37
Nagatoro	1.7	1.5-1.7	0.12	0.26-0.32
Kumagaya	1.0	1.2-1.5	0.11	0.11-0.14
Urawa	1.6	1.0-1.2	0.12	0.12-0.30
Yotsugi	3.6	3.6-4.0	0.10	0.15-0.17

reduce antimony(V) to antimony(III).

2.6 Tin(5)

A large volume of the sample water was preconcentrated with sulfuric acid to prevent of hydrolysis of tin. Interference from copper and iron was eliminated by extracting copper with a carbon tetrachloride solution of zinc dibenzyl dithiocarbamate and by complexing iron with 1,10-phenanthroline, insted of the Chelex separation.

3. Analytical results

Table 1 shows the analytical results of trace elements in River Arakawa collected at several sites. The higher concentrations of arsenic, selenium, antimony and copper at Mitsumine could be due to the dissolution of ores which were formerly produced at Chichibu Mine above Mitsumine. The water is diluted by an increased volume of water mid-stream but the concentrations increase again downstream. All the results are within the new Standards for city water quality. Table 2 shows the chronological change of arsenic and selenium in River Arakawa. There is no appreciable change in Table 2.

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