

SPECIFIC DETERMINATION OF TRACE AMOUNT OF IRON IN DIFFERENT OXIDATION STATE IN NATURAL WATER

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Niigata, Niigata University
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Niigata Area



- Niigata is located in the center of Japan Sea coast.
- The population is about 80 hundred thousand.
- Average Annual Temperature is 14.7 °C.
- 80 % of Niigata prefecture receives an average maximum snow accumulation of over 1 meter.
- Snowfall is heavy in the southern part of Niigata.

Snow accumulation at Tsunan



Niigata University (Ikarashi Campus)

Why do we have to make Iron speciation?

- ▶ The behavior of dissolved iron species in natural waters has not been well understood.
- ▶ The information on their chemical forms may foster better understanding of iron geochemistry.
- ▶ The relationship between the concentration of iron complex with organic compounds and ISOYAKE (Sea Desert or Coralline flats).

Speciation method for trace metal ions

- Spectrophotometry
 - Absorptiometry,
 - Furuorometry
 - insufficient sensitivities for target chemical components present at sub- $\mu\text{g dm}^{-3}$ to $\mu\text{g dm}^{-3}$ concentration levels
 - Some troublesome pre-concentration steps, which may also cause species alteration are required.
- Instrumental analytical methods
 - GFAAS
 - ICP-AES
 - ICP-MS $\text{Ar}_{40}\text{O}_{16}$
 - Some mutual separation steps, which may cause species alteration are required.

What is FI-SPS method?

Flow Injection Solid Phase Spectrometry

- Formation of colored or fluorescent complex of target metal ions in a flow system.
- Concentration of target metal complex on small amount of solid particles (*e.g.* ion exchanger) in a Flow-through cell.
- Direct measurements of the degree of light absorption (or the intensity of the light emitted) by the solid phase.

Characteristics of FI-SPS method

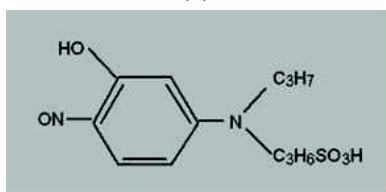
- FI-SPS method is based on the chemical reaction.

It does not need some troublesome separation steps which may cause species alteration.

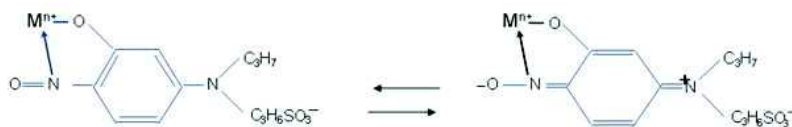
- High sensitivity.

Only by using a few cm^3 of sample solution, the concentration of sample components present less than $1 \mu\text{g dm}^{-3}$ can easily be measured without using any expensive apparatus. It also does not need some troublesome pre-concentration steps which may cause species alteration.

Nitroso-PSAP (1)



2-nitroso-5-[*N*-*n*-propyl-*N*-(3-sulfopropyl) amino]phenol
(nitroso-PSAP or *N*-PSAP)



Charged quinone structure of PSAP complex

Molar absorptivity is in the $10^4 - 10^5$ order

High sensitive coloring reagent for metal for metal ions

Reduction of the Fe(III)-PSAP complex

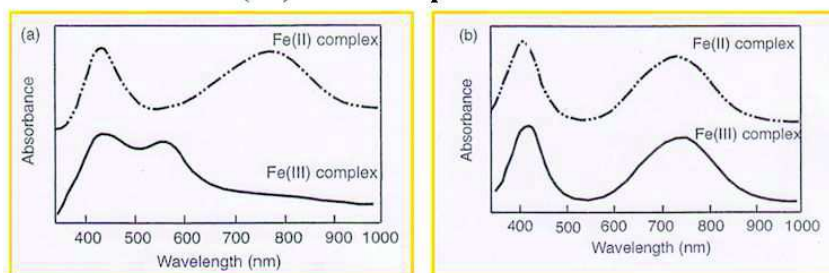


Fig. Absorption spectra of Fe(II) and Fe(III) complexes in solution (a) and in solid phase (b) at pH 7.0.

Fe(III) complex in anion exchanger is easily reduced to the Fe(II) complex without any reducing agents.

Characteristics of Nitroso-PSAP complex

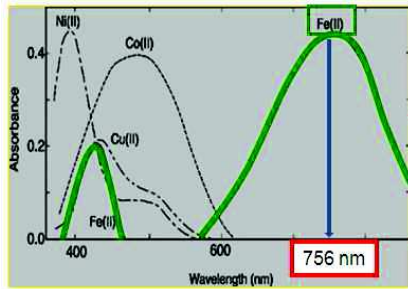


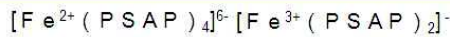
Fig. Absorption spectra of PSAP complex with some metal ions in solution

N-PSAP is used as a selective and sensitive spectrophotometric reagent for the determination of iron(II) in water samples

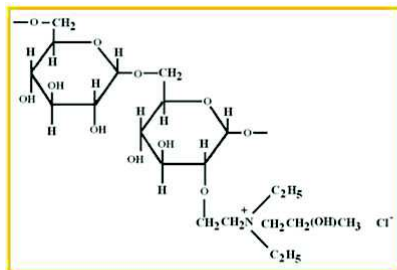
Metal ion	Fe (II)	Fe (III)	Ni(II)	Cu(II)	Co (II)
Molar absorptivity / mol ⁻¹ dm ² cm ⁻¹	4.0×10 ⁴	4.0×10 ⁴	2.8×10 ⁴	2.0×10 ⁴	4.5×10 ⁴
Optimum pH for complex formation	6.5~10.5	6.5~10.5	6~10	6~10	4~8
Composition (metal : reagent)	1 : 4	1 : 2	1 : 2	1 : 2	1 : 3

Acid dissociation constants
pKa₁ = 2.74 pKa₂ = 8.45

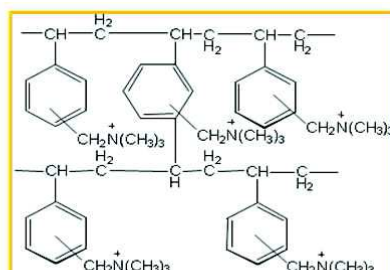
Charge of *N*-PSAP (pH4~10)
-2



Anion exchanger



QAE-Sephadex anion exchange gel



Dowex I anion exchange resin

- ✓ Although this reduction reaction of the Fe(III) complex proceeded in solution, its reaction rate is very slow.
- ✓ Reduction reaction of Fe(III)-PSAP complex occurs in both anion exchanger phase
- ✓ The reduction is accelerated only in the anion exchanger phase.

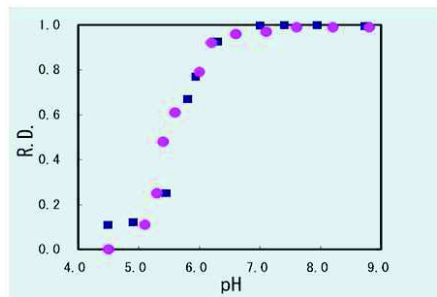
Reduction of the Fe(III)-PSAP complex in various conditions

▶ **No effects on the reduction reaction**

- Type of anion exchanger,
- Concentration of PSAP
- Kind of buffer solution
- UV radiation

▶ **Grate effect**

pH (4~9)



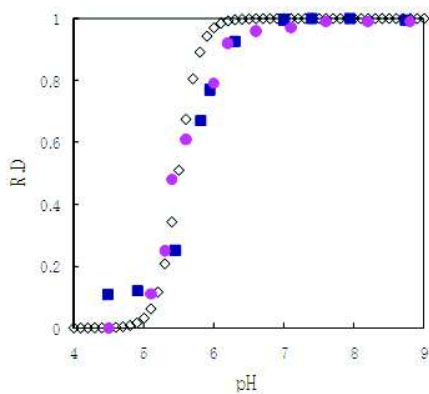
The reduction degree (R.D.) : the extent of reduction of the Fe(III)
 R.D. = 1 : Fe(III)-PSAP complex in anion exchanger phase is completely reduced.
 R.D. = 0 : reduction reaction does not take place.

- QAE-Sepadex A25,
- Dowex I-X2

Fig. Effect of pH on the reduction of Fe(III) complex in the anion exchanger phase.

Mechanism of reduction of the Fe(III)-PSAP complex in solid phase

$$R.D. = \left\{ 1 + \left(\frac{\beta_{2Fe^{3+}}}{\beta_{4Fe^{2+}}} \right) \times \alpha [L^{2-}]^2 \left(10^{\frac{-E^{**} + 0.059 \log \alpha - 0.059 \text{pH}}{0.059}} \right) \right\}^{-1}$$



- QAE-Sephadex A-25
- Dowex I-X2
- ◇ Calculated R.D. (E** = 0.08V)

The experimental values were approximately on the calculated curve as E** = 0.08

FI-SPS system

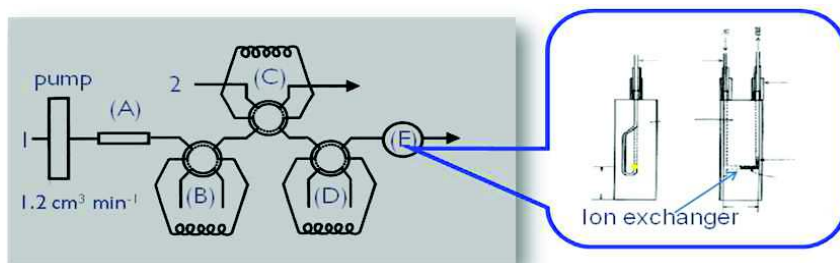
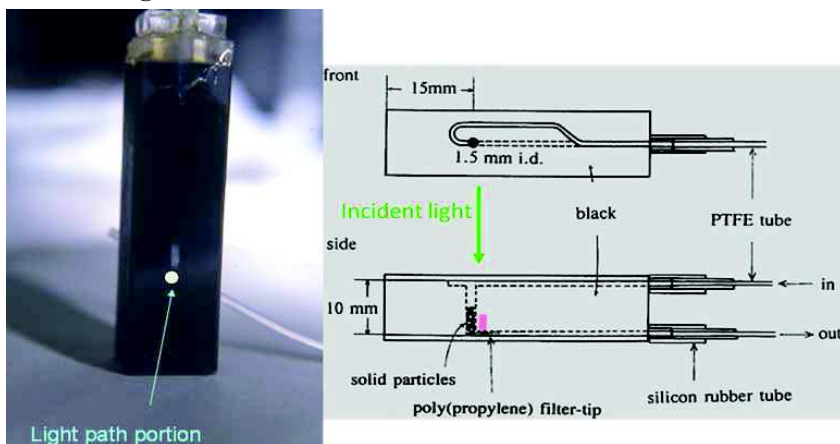


Fig. Schematic flow system diagram for simultaneous determination of Fe(II), total Fe and Co(II). (A): On-line column packed with Chelex 100 (2 mm i.d., 10 cm long), (B): Six-way rotary valve for desorbing agent solution introduction ($2 \text{ mol dm}^{-3} \text{ NH}_4\text{NO}_3$ and 30 % (v/v) acetone), (C): Six-way rotary valve for sample solution introduction with a 3.2 cm^3 PTFE tube loop, (D): Six-way rotary valve for the HEPES buffer solution introduction (pH 7.3) with a 15.8 cm^3 PTFE tubeloop, (E): Flow-through cell packed with QAE-Sephadex anion-exchange gel.

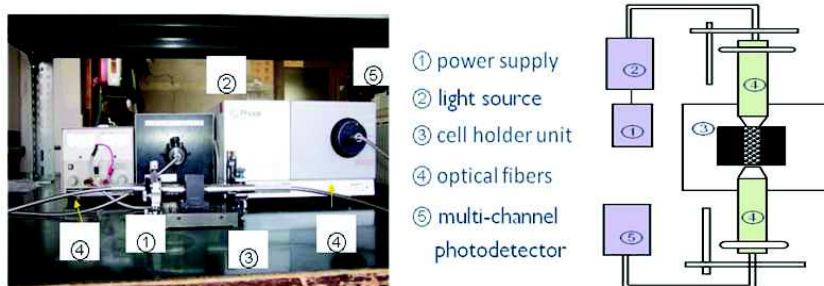
(1): Acetate buffer solution (pH 4.5), (2) HEPES buffer solution (pH 7.3).

Flow-through cell for FI-SPS



Light measurement

- iodine lamp (150 W) as the light source
- multi-channel photodetector
- bundle of optical fibers (200 mm i.d.)



The continuous measurements of the difference between the attenuances at two different wavelengths resulted in an effective suppression of the background attenuance change due to the shrinkage of the ion exchanger.

Color development profile

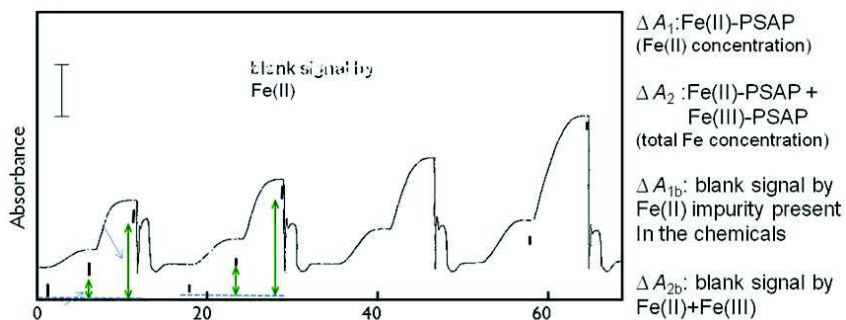


Fig. Colour development profiles of Nitroso-PSAP complexes adsorbed on the QAE-Sephadex. Sample volume; 4.0 cm³. (A) Blank solution. (B) Fe(II) 0.5 μg dm⁻³, Fe(III) 0.5 μg dm⁻³. (C) Fe(II) 1.0 μg dm⁻³, Fe(III) 1.0 μg dm⁻³. (D) Fe(II) 1.5 μg dm⁻³, Fe(III) 1.5 μg dm⁻³. (E) HEPES buffer solution (pH 7.3). (F) Desorbing agent solution.

Sensitivity and Detection Limit

Total Fe : $\Delta A_2 = 0.0658 X + 0.0988$ $r = 0.998$

Fe(II) : $\Delta A_1 = 0.0416 X + 0.0343$ $r = 0.994$

(X is the sample concentration in μg dm⁻³)

Sensitivity $\left. \begin{array}{l} \text{Total Fe : 100 times} \\ \text{Fe(II) : 60 times} \end{array} \right\}$

higher than that of the corresponding solution method (light-path length : 1 cm),

Total Fe : $\Delta A_2 = 0.0658 X + 0.0988$ $r = 0.998$

Fe(II) : $\Delta A_1 = 0.0416 X + 0.0343$ $r = 0.994$
(X is the sample concentration in $\mu\text{g dm}^{-3}$)

Detection limit (3σ) 0.18 ng for Fe(II),
0.18 ng for total Fe
(Sample volume: 3.2 cm^3 , $n = 10$)

The present method has sufficient sensitivity to determine the concentration of iron present at sub- $\mu\text{g dm}^{-3}$ levels.

Effect of co-existing ions

Table Effect of co-existing ions on the determination of respective metal ions.

Ion	Concentration ($\mu\text{g dm}^{-3}$)	Error (%) Fe(II)($0.4 \mu\text{g dm}^{-3}$)
Al(III)	1000	+2.8
Ca(II)	2000	-2.0
	5000	+1.5
	10000	-9.0
Cu(II)	2	-3.9
	5	-2.4
	20	+1.0
Mg(II)	500	0
	4000	+2.8
	8000	+1.5
Ni(II)	2	-3.2
	10	-1.9
	20	-1.2
Zn(II)	2	-1.4
	5	-3.0
	5 ^a	-3.0

Precision

Table. Determination of Iron in reference rock sample and synthetic Mixture sample

Sample	Fe concentration/%	Certified value/ %
JR-2	0.51 ± 0.01 as total Fe ($n = 5$)	0.53 as total Fe
Synthetic mixture sample	0.67 ± 0.03 for Fe(II) ($n = 4$) 1.07 ± 0.04 for total Fe ($n = 4$)	$0.66 \mu\text{g dm}^{-3}$ for Fe(II) $0.42 \mu\text{g dm}^{-3}$ for Fe(III)

Standard addition method**Table** Standard addition method on Fe(II) and Fe(III) ions in natural water

Sample ^a	Fe(II) _{added} (ng)	Fe(II) _{found} (ng)	Recovery (%)	Fe(III) _{added} (ng)	Fe total _{found} (ng)	Recovery (%)
Gorge water 1	0	1.45	—	0	8.13	—
	2.40	3.76	96	4.87	13.2	102
	4.79	6.13	98	9.73	18.2	102
Gorge water 2	0	0.49	—	0	2.15	—
	0.60	1.08	98	2.47	4.83	105
	1.20	1.71	102	4.94	6.75	95
	1.80	2.23	97	7.41	9.73	102

^a Sample volume introduced: 3.2 cm³.

Conclusion

- A novel determination method for iron, in which QAE-Sephadex anion exchanger packed in a flow-through cell is used as a medium not only for concentration but also for reduction of the target metal ions.
- The detection limits (3s) were 0.18 ng for Fe(II), 0.18 ng for total.
- The present method is applicable to the determination of dissolved iron species present at mg dm⁻³ without any preconcentration steps.
- The dissolved Fe(II) in gorge water was at redox equilibrium with amorphous Fe(OH)₃.
- The concentration of the dissolved Fe(III) was much higher than that calculated only by the solubility of amorphous Fe(OH)₃.
- The Fe(III) dissolved in gorge water was controlled by the solubility of amorphous Fe(OH)₃, in the presence of organic matters such as humic acid.