

AAS

APPLICATION NOTES

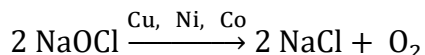
The determination of copper, nickel and cobalt in sodium hypochlorite

AAS



Introduction

Copper, nickel and cobalt are highly deleterious to sodium hypochlorite by catalysing the oxygen forming decomposition, viz:



Sodium hypochlorite manufactured at Botany has gassing rates around 8 mL O₂/300g/20h @ 37°C.

Contamination by Cu, Ni or Co increases this gassing rate by approximately the following amount:

Contaminant	Increase in gassing rate
10 µg/L Cu	1 mL/300g/20 h @ 37°C
10 µg/L Ni	15 "
10 µg/L Co	8 "

This method has been designed to detect the cause of high gassing rate sodium hypochlorite. Flame AAS is used for the Cu determination and graphite furnace AAS for Ni and Co. Detect limits are approximately as follows:

Cu	5 µg/L
Ni	5 µg/L
Co	1 µg/L

As such low levels of detection, blanks become significant, and it is stressed that all equipment be acid washed before commencing, to reduce contamination to a minimum.

The sample is decomposed with hydrogen peroxide, the pH adjusted to 4.5 – 5, copper, nickel and cobalt are double extracted with 0.1M 8-hydroxyquinoline in chloroform, and the chloroform is evaporated off on a hot plate. The residues are dissolved in dilute hydrochloric acid and determined by AAS. Metal standard is added to the extracted material and again double extracted. The four extracts are run separately to check extraction efficiencies and are compared with an aqueous standard.

Investigation of the “% extraction vs pH” curves for the three metals were not deemed necessary during the development of this method as the method includes an internal check which indicates that proper extraction is taking place. The ratio of absorbances of the two extracts for each of the sample and standard extracts indicates the efficiency (e.g. extract 1/extract 2 = 2 indicates 75% extraction for 2 extracts and extract 1/extract 2 = 10 indicates 99% extraction for 2 extracts). It is obvious that a high ratio of absorbances of extract 1 to extract 2 indicates good extraction.

Apparatus

A GBC atomic absorption spectrophotometer and a GBC automated graphite furnace system.

1	5 µL pipettor
50	200 µL pipettor
200	1000 µL pipettor
	PTFE beaker, 250 mL
	pH meter

General reagents

1. Ammonium hydroxide, A.R. grade.
2. Chloroform, A.R. grade.
3. Cobalt metal, A.R. grade 99% min.
4. Copper metal, A.R. grade 99% min.
5. Hydrochloric acid, A.R. grade, 36% w/w.
6. Hydrogen peroxide, A.R. grade, 30% (100 volume).
7. 8-Hydroxyquinoline, A.R. grade.
8. Nickel metal, A.R. grade, 99% min.
9. Nitric acid, concentrated, A.R. grade.
10. Potassium hydrogen phthalate, A.R. grade.

Special reagents

1. Ammonium hydroxide, 4M.
Dilute 142 ± 1 mL concentrated ammonium hydroxide to 500 mL with distilled water.
2. Cobalt Stock Solution, 1000 $\mu\text{g Co/mL}$.
Dissolve 1.000 g cobalt metal in a mixture of 10 mL distilled water and 10 mL concentrated nitric acid. Dilute to 1000 mL with distilled water and mix well.
3. Copper Stock solution, 1000 $\mu\text{g Cu/mL}$.
Dissolve 1.000 g copper metal in a mixture of 10 mL distilled water and 10 mL concentrated nitric acid. Dilute to 1000 mL with distilled water and mix well.
4. 8-Hydroxyquinoline, 0.10 M in Chloroform.
Into a brown reagent bottle, weigh 2.90 ± 0.05 g 8-hydroxyquinoline, dissolve and dilute to 200 mL with chloroform.
5. Nickel Stock solution, 1000 $\mu\text{g Ni/mL}$.
Dissolve 1.000 g nickel metal in a mixture of 10 mL distilled water and 10 mL concentrated nitric acid, using gentle heating. When dissolution is complete, dilute to 1000 mL with distilled water and mix well.
6. Mixed Standard, 25 $\mu\text{g Cu}$, 5.0 $\mu\text{g Co}$, 5.0 $\mu\text{g Ni/mL}$.
Into a 25 mL volumetric flask add:
625 μL copper stock solution,
125 μL cobalt stock solution,
125 μL nickel stock solution,
Add 5 drops concentrated nitric acid and dilute to 25 mL with distilled water. Renew weekly.
7. Potassium hydrogen phthalate, buffer solution, 0.25 molar
Dissolve 12.77 ± 0.01 g potassium hydrogen phthalate in distilled water and dilute to 250 mL.

Procedure

NOTE:

The following apparatus must be cleaned with concentrated A.R. HCl followed by distilled water before the test.

- a) PTFE beaker.
 - b) 250 mL separating funnel.
 - c) 6 off 50 mL beakers.
 - d) 50 mL measuring cylinder.
 - e) 5 mL measuring cylinder.
1. Into a 250 mL PTFE beaker, transfer 50 ± 1 mL sodium hypochlorite sample solution.
 2. Add very slowly with swirling, 15 ± 0.5 mL hydrogen peroxide solution.
 3. To a 50 mL beaker labelled “blank” add 15 ± 0.5 mL hydrogen peroxide solution and boil gently to dryness.
 4. To sample from step 2 above, add 20 drops concentrated hydrochloric acid and ensure pH of the solution is less than 2. If not, continue adding (and counting the drops) concentrated hydrochloric acid drop-wise until pH is less than 2.
 5. Add the number of drops of HCl used in step 4 to the “blank” beaker in step 3 and evaporate to dryness.
 6. Add to sample beaker from step 4, 2.0 ± 0.2 mL potassium hydrogen phthalate buffer solution and adjust pH to 4.5 to 5.0 using drop-wise additions of 4 M ammonium hydroxide. Count the drops required.
 7. When “blank” beaker has been boiled to dryness add the number of drops of 4 M ammonium hydroxide used in step 6 and again boil to dryness.
 8. Transfer sample from step 6 into a 250 mL separating funnel and extract with 10.0 ± 0.1 mL 0.1 M 8-hydroxyquinoline solution, shaking for 1 minute.
 9. When layers have separated, transfer chloroform layer to a clean 50 mL beaker. Label as S1 (sample 1st extract).
 10. Re-extract with a second 10.0 mL portion again shaking for 1 minute and run extract into another 50 mL beaker. Label as S2 (sample 2nd extract).
 11. To the extracted material in separating funnel add 100 μ L mixed standard and extract twice with 10.0 mL 8-hydroxyquinoline, shaking for 1 minute. Run the extracts into separate 50 mL beakers labelled ST1 (standard 1st extract) and ST2 (standard 2nd extract).
 12. Place the four 50 mL beakers on a hot plate and evaporate off the chloroform until only the molten 8-hydroxyquinoline remains.
 13. To the blank beaker from step 7 add 10.0 mL 8-hydroxyquinoline and evaporate off the chloroform as in step 12.
 14. To all five beakers in steps 12 and 13, add 5.0 mL distilled water containing 5 drops concentrated hydrochloric acid and swirl until the 8-hydroxyquinoline has dissolved.
 15. Prepare AA standard as follows:
Into a 50 mL beaker add 100 μ L mixed standard and 4.9 mL distilled water containing 5 drops concentrated hydrochloric acid. Mix well. This solution contains 0.5 μ g Cu/mL, 0.1 μ g Ni/mL and 0.1 μ g Co/mL.
 16. For nickel and cobalt, use the operating parameters and furnace programs shown in Figure 1. Determine the metals in duplicate (using peak height mode and reading in absorbance) using the following sequence:

No injection	(= clean of furnace)
5 µL blank	
5 µL S2	Sample 2 nd extract
5 µL ST2	Standard 2 nd extract
5 µL S1	Sample 1 st extract
5 µL ST1	Standard 1 st extract
5 µL aqueous standard	

NOTE:

- Plotting of the peak shape is advised for each injection to ensure that any spurious peaks are not being measured by the instrument.**
- Any sample injections giving peak heights greater than the aqueous standard should be re-run using an appropriately smaller injection.**

- Determine copper by flame AAS using an air-acetylene flame and the operating parameters shown in Figure 1. Calibrate against aqueous standards and read in concentration units.

Calculation

- Verification of proper extraction. Calculate, for each of the three metals, % recovery for added standard as follows:

$$\% \text{ recovery, } R = \frac{(ST1 + ST2) \times 100}{AS}$$

If % recovery is greater than 80%, this is satisfactory. Then,

- Ni/Co

Metal concentration, (µg/L)

$$= \frac{(S1 + S2 - B) \times 0.1 \times 5.0 \times 1000 \times 100}{AS \times 50 \times R}$$

$$= \frac{(S1 + S2 - B) \times 1000}{AS \times R}$$

- Cu

Cu concentration, (µg/L)

$$= \frac{(S1 + S2 - B) \times 0.5 \times 5.0 \times 1000 \times 100}{AS \times 50 \times R}$$

$$= \frac{(S1 + S2 - B) \times 5000}{AS \times R}$$

Where S1 = reading of sample (1st extract) S2 = reading of sample (2nd extract)
 B = reading of blank AS = reading of aqueous standard
 ST1 = reading of standard (1st extract) ST2 = reading of standard (2nd extract)
 R = % recovery of added standard

and readings are in absorbance for Ni/Co and in concentration for Cu.

Results

Two samples were analyzed. Sample 1 was from a production batch of sodium hypochlorite. Sample 2 was a sample from the same batch spiked with 50 µg/L Cu, 10 µg/L Ni and 10 µ/L Co. The results are shown in Tables 1 and 2. Note that readings are in absorbance units for Ni/Co and in concentration units for Cu.

	Ni (furnace)	Co (furnace)	Cu (flame)
B	0.005	0.000	0.042
S2	0.000	0.064	0.032
ST2	0.020	0.027	0.063
S1	0.068	0.468	0.158
ST1	0.161	0.469	0.459
AS	0.243	0.494	0.5
R	75%	100%	104%
Conc. µg/L	3	11	14

Table 1: Results for Sample 1

	Ni (furnace)	Co (furnace)	Cu (flame)
S2	0.020	0.090	0.070
ST2	0.000	0.073	0.048
S1	0.348	0.829	0.592
ST1	0.214	0.334	0.445
AS	0.243	0.494	0.5
R	88%	82%	99%
Conc. µg/L	17	23	63

Table 2: Results for Sample 2

Recoveries were acceptable in all cases and, considering the very low concentrations (Ni was near the detection limit), the agreement of the measured concentrations for Sample 2 with concentrations added was also acceptable.

Cu Operating Parameters				
Element:	Cu		Wavelength:	324.8 nm
Slit Width:	0.5 nm		Atomization:	Air-Acetylene
Lamp Current:	3.0 mA		EHT (gain):	- 384 V
Scale Expansion:	1.000		Integration Time:	3 s
Double Beam				

Ni Operating Parameters				
Element:	Ni		Wavelength:	232.0 nm
Slit Width:	0.2 nm		Atomization:	Furnace
Lamp Current:	10.0 mA		EHT (gain):	- 504 V
Scale Expansion:	1.000		Integration Time:	0.02 s
Double Beam				

Ni Graphite Furnace Parameters						
Step Number	Final Temp. (°C)	Ramp Time (sec)	Hold Time (sec)	Inert Gas	Aux. Gas	Read On
1	75	1.0	0.0	No	No	No
2	90	3.0	0.0	No	No	No
3	110	20.0	10.0	No	No	No
4	700	5.0	10.0	Yes	No	No
5	2400	1.0	2.0	Yes	No	Yes

Co Operating Parameters				
Element:	Co		Wavelength:	240.7 nm
Slit Width:	0.2 nm		Atomization:	Furnace
Lamp Current:	6.0 mA		EHT (gain):	- 524 V
Scale Expansion:	1.000		Integration Time:	0.02 s
Double Beam				

Co Graphite Furnace Parameters						
Step Number	Final Temp. (°C)	Ramp Time (sec)	Hold Time (sec)	Inert Gas	Aux. Gas	Read On
1	75	1.0	0.0	No	No	No
2	90	3.0	0.0	No	No	No
3	110	20.0	10.0	No	No	No
4	700	5.0	10.0	Yes	No	No
5	2400	1.0	2.0	Yes	No	Yes

Figure 1: Operating parameters for Cu, Ni and Co

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