

STABILIZED HYDROXYLAMINE SOLUTIONS

DESCRIPTION

5

BACKGROUND OF THE INVENTION

Field of the Invention

10 This invention relates to a stabilized hydroxylamine solution, and more particularly, to a hydroxylamine solution, which comprises a selected stabilizer.

Description of the Related Art

15

Hydroxylamine, especially in the form of its salts with sulfuric acid, hydrochloric acid and others, is an important intermediate for the chemical industry, and is widely employed in chemical syntheses. It is frequently necessary to employ hydroxylamine in the form of a solution of the free base, which is generally liberated from a hydroxylammonium salt such as, for example, hydroxylammonium sulfate or hydroxylammonium chloride, by the action of an appropriate base, such as ammonia, sodium hydroxide solution or an alcoholate. Neutral and alkaline hydroxylamine solutions are unstable and decompose to form ammonia, nitrogen, oxides of nitrogen and water, so that their transportation or storage is highly problematic. The rate of decomposition increases with rising temperature, rising hydroxylamine concentration, rising pH and rising concentration of catalytically active impurities.

In Order to avoid the decomposition of the hydroxylamine, a stabilizer is added to the solutions. Numerous stabilizers for hydroxylamine are already known. Proposals which have been made are: thioglycolic acid (JP-A-58069843), glycerol monethers and ethylene oxide adducts thereof (DE-A-29 19 554), hydroxyanthraquinones (DE-A-33 43 600), hydroxyquinolines (DE-A-33 45 734), polyhydroxyhexano-1,4-lactone (DE-A-33 45 733), anthocyanins (DE-A-33 47 260), hydroxyquinaldines, flavones, benzonitrile, N-phenyl-N hydroxythiourea (DE-A-36 01 803), flavans (DE-A-33 43 599), thiosulfates, mercaptobenzothiazoles, mercaptoalkanol, mercaptothiazolines, thiuram disulfides, thioureas (EP-A-516 933), the tetrasodium salt of ethylenediaminetetraacetic acid, the trisodium salt of N-hydroxyethylenediaminetriacetic acid, polyvinylpyrrolidone or poly-N-vinyl-5-ethyl-2-oxazolidinone (U.S. Patent No. 3,145,082), amide oximes (U.S. Patent No. 3,480,391), hydroxamic acids (U.S. Patent

No. 3,480,391), hydroxyureas (U.S. Patent No. 3,544,270), dipyridyl compounds (JP-A-58069842), aminoquinolines (JP-A-58069844), phenanthrolines (JP A-58069841), and polyhydroxyphenols (JP-A-4878099).

5

However, none of the stabilizers proposed to date has been able to provide hydroxylamine solutions with sufficient stabilization to prevent excessive decomposition of the hydroxylamine to occur, especially during storage.

10

What is desired and needed is a better means for stabilizing a hydroxylamine solution.

DETAILED DESCRIPTION OF THE INVENTION

15

This Invention relates to a stable hydroxylamine solution, and more particularly, to such a solution, which comprises a selected stabilizer.

20 Hydroxylamine is prepared commercially by the Raschig process or variations thereof, in which ammonium or sodium nitrite is reacted in aqueous solution with ammonium or sodium bi-sulfite and sulfur dioxide. The resulting disulfonate salts are subsequently hydrolyzed to a solution containing essentially

25 hydroxylammonium sulfate, sulfuric acid, ammonium sulfate and/or sodium sulfate plus minor amounts of the corresponding nitrate. This solution can be used, after neutralization with a base, as a source of hydroxylamine or pure hydroxylammonium salts from the mixture.

30

A suitable selected stabilizer is selected. A suitable selected stabilizer is a compound which complexes or chelates metals, such as for example, Ca, Fe, Zn, Al, Cu, Ni, etc., which catalyze the decomposition of an aqueous hydroxylamine solution during

35 its manufacture, storage and transportation. Such a stabilizer includes (a) diethylenetriaminepentaacetic acid ("DPTA"),

(b) triethylenetetraminehexaacetic acid ("TTHA"), (c) ethylene-bis(oxyethylenetriamino)tetraacetic acid ("EGTA"), (d) 1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetraacetic acid, (e) 4,8-di-

40 hydroxyquinoline-2-carboxylic acid, (f) 4,5-dihydroxy-1,3-benzene-disulfonic acid, (g) 4,7-dihydroxy-1,10-phenanthroline,

(h) 2-mercaptopyridine-3-carboxylic acid, (i) bis[N,N'-bis(carboxymethyl)-aminomethyl]fluorescein [fluorexon], (j) N,N-bis(2-carboxyethyl)-N,N'-ethylenediglycine trihydrate, (k) Cystine, (l) 2,3-di-

45 hydroxybenzoic acid, (m) Thiosalicylic acid, (n) a mixture of the any of the foregoing compounds and (n) and the salts of any of the foregoing compounds. Particularly preferred salts of the

3

selected stabilizers include amine salts, e.g. triethylamine, triethanolamine; hydroxyamines; acid addition salts with inorganic acids, e.g. HF, HCl, HBr, H₂SO₄, H₃PO₄, etc., if basic functions are present.

5

The selected stabilizer is added or combined either with the reactants during the process for manufacturing the hydroxylamine solution, or during the storage of a basic or neutralized aqueous solution of such manufactured hydroxylamine.

10

The selected stabilizer is added to the reactants, e.g. Raschig process reactants, or to a neutral or basic aqueous hydroxylamine solution, e.g. in excess of 50-weight percent hydroxylamine solution, in an amount sufficient to stabilize the hydroxyl-

15 amine solution. By "stabilize" is meant that the hydroxylamine concentration in the neutral or basic solution does not decompose or decrease by 2.0 weight percentage in a time period of 24 hours at a temperature of 25°C. Typically, the final concentration of the added selected stabilizer is present in the resultant neutral
20 or basic hydroxylamine solution in an amount ranging from about 0.005 percent to about 0.1 percent by weight to the total weight of the resultant solution. In this regard, the concentration of hydroxylamine is in general 1-100% by weight, in particular 1-70% by weight, based on the overall weight of the resultant solution.

25

It is to be pointed out that the selected stabilizer can be used as a single selected stabilizer or as a mixture of at least two selected stabilizers. Additionally, the selected stabilizer or stabilizers (mixture) can be combined with other well known
30 stabilizer, such as, thioglycolic acid, glycerol monethers and ethylene oxide adducts thereof, hydroxylanthroquinones, hydroxyquinolines, polyhydroxyhexano-1,4-lactone, anthocyanins, hydroxyquinaldines, flavones, benzonitrile, N-phenyl-N-hydroxythiourea, flavans, thiosulfates, mercaptobenzothiazoles, mercaptothiazolines, thiuram disulfides, thioureas, the tetrasodium salt of
35 ethylenediaminetetraacetic acid, the trisodium salt of N-hydroxyethylethylenediaminetriacetic acid, polyvinylpyrrolidone or poly-N-vinyl-5-ethyl-2-oxazolidinone, amide oximes, hydroxamic acids, hydroxyureas, dipyridyl compounds, aminoquinolines,
40 phenanthrolines, and polyhydroxyphenols. In this regard, reference is also made to U.S. Patent 5,783,161, which reveals other stabilizers.

45

4

Stabilizer for H-Base
Weight Loss Screening Test
Hydroxylamine (HA) and Ammonia Determination after
Weight Loss Screening Test

5

	1997 stabilized 56% HA + Fe(III) + Candidate	Wt loss g	% wt loss	% HA remaining after screening test	% ammonia formed during screening test	comment
10	Diethylenetriaminepentaacetic acid	0	0	56	0	
	Triethylenetetraminehexaacetic acid (TTHA)	0	0	55	0	
	Ethylenebis(oxyethylenitrilo)tetra- acetic acid (EGTA)	0	0	52	0	
15	1,4,8,11-tetraazacyclotetradecane- 1,4,8,11-tetraacetic acid	0	0	54	0	
	4,8-dihydroxyquinoline-2-carboxylic acid	0	0	54	0	
	4,5-dihydroxy-1,3-benzenedisulfonic acid	0	0	54	0	Rose color
20	Thiosalicylic acid	0	0	54	0	Light yellow
	Salicylic acid	0.26	21	18	3.4	Light yellow
	2-mercaptonicotinic	0	0	54	0	
25	2-carboxyethylphosphonic acid	0.2	16	19	4.7	
	cystine	0	0	52	1.1	
	4,7-dihydroxy-1,10-phenanthroline	0.01	0.8	51	1.1	Redish color
30	1,4,8,11-tetraazacyclotetradecane- 5,7-dione	0.06	4.9	42	3.2	
	Fluorexon or {bis[N,N-bis(carboxy- methyl)-aminomethyl]fluorescein}	0.01	0.8	54	0	color
	1997 stabilized 55% HA "no candidate"	0.34	28	16	2.2	
35	CDTA	0	0	55	0	
	N,N'-bis(2-carboxyethyl)- N,N'-ethylenediglycine trihydrate	0	0	55	0	
	Inositolhexaphosphoric acid	0.12	10	28	5	
	2,3-dihydroxybenzoic acid	0.02	1.6	50	1.6	Some loss of sample before titration

40

45

Gas Evolution Method

General Procedure: 4 mL glass vial on Top Loading Balance,
 2 mL of Fe(III) [356 mg Fe(III) Sulfate-Hydrate / 10 mL H₂O
 5 $\approx$ 5000 ppm Fe(III)] add to 10 mL plastic beaker with micro
 stirrer, 100 mL of water or new stabilizer usually at 10000 ppm,
 1 mL of either stabilized oder destabilized HA (1997 56%)
 contents transferred to glass vial + wt loss monitored vs. Time

min.	1997	destabilized	1997 destabilized 2,6-Pyridinedicarboxylic acid	1997 stabilized H ₂ O
0	6.07	wt loss	0 6.02	0 6.01
1	6.06		5 6.01 .01	3 6.03 0.01
2	6.06	.01	10 5.99 .03	5 5.98 0.06
5	5.98	.09	12 5.99 .03	6 5.90 0.14
7	5.93	.14	14 5.97 .05	10 5.77 0.27
11	5.91	.16	17 5.57 .05	11 5.77 0.27
18	5.90	.17	18 5.96 .06	12 5.76 0.28
21	5.89	.18	23 5.95 .07	13 5.77 0.27
24	5.89	.18	29 5.94 .08	14 5.76 0.28
30	5.88	.19	33 5.93 .09	20 5.76 0.28
36	5.88	.19	43 5.91 0.11	26 5.75 0.29
40	5.88	.19	54 5.91 0.11	30 5.25 0.29
51	5.87	0.20		42 5.74 0.30
61	5.86	0.21		

25

Destabilization procedure - Pass 200 mL of 1997 56% HA through
 large anion column, collect effluent / Fraction every 50 mL.

30

35

40

45

Gas Evolution

	2 mL	5000 ppm Fe(III)	U4A15 1.63 mg	U4A13 1.98 mg	U4A9 2.21 mg	1997 SW 2.02	U4AW 1.5
5	100 mL	H ₂ O or Stabilizer	99.18 mg 10,000 ppm	99.9	100.2 mg	99.9 water	99.2
	1 mL	HA	1189.9 mg	1170 mg	1173 mg	1199	1182
	Vial		4.90 g	4.85	4.85	4.88	4.81
10			1 6.04	1 5.86	1 5.95 0	6.02 1 6.02	1 5.97 0
			2 6.04 3 6.03 0.01	2 5.82 0 3 5.87 -0.01	2 5.95 0 3 5.95 0	2 6.02 0 3 6.00 0.02	2 5.97 0 3 5.96 0.01
			4 6.02 0.02 5 5.99 0.05	4 5.87 -0.01 5 5.87 -0.01	4 5.95 0 5 5.95 0	4 5.95 0.07 5 5.86 0.16	4 5.95 0.02 5 5.92 0.05
15			6 5.95 0.01 7 5.93 0.11	6 5.87 -0.01 7 5.87 -0.01	6 5.95 0 7 5.95 0	6 5.79 0.03 7 5.78 0.24	6 5.89 0.05 7 5.85 0.12
			8 5.91 0.13 9 5.91 0.13	8 5.87 -0.01 9 5.87 -0.01	8 5.95 0 9 5.95 0	8 5.77 0.25 9 5.76 0.26	8 5.82 0.15 9 5.82 0.15
20			10 5.90 0.14 11 5.90 0.14	10 5.86 0 11 5.86 0	10 5.95 0 12 5.95 0	10 11 5.75 0.27	10 5.81 0.16 11 5.81 0.16
			15 5.88 0.16 29 5.87 0.17	15 5.87 -0.01 29 5.87 -0.01	15 5.95 0 29 5.94 0.01	35 5.73 0.29	15 5.80 0.17 31 5.78 0.19

- U4A15 = U destabilized 1997 56%, 4 Fraction #4 150-200 mL,
 25 A = 1st destabilized, 15 = 1,4,10,13 tetroxa-7,16-
 diazabyclooctadecene 104.3 mg/10 mL 29,580-9
- U4A13 = U destabilized, ect, ect, 13 = 4,5-dihydroxy-1,3
 benzene disulfonic acid, disodiumsalt
 106.3 mg/10 mL 12,255-3
- 30 U4A9 = U destabilized, 9 = 1,4,8,11 Tetraazacyclotetra-
 decane-1,4,8,11-tetraacetic acid 100.9 mg/10 mL H₂O
 40,040 mg
- 1997SW = stabilized, water
- U4AW = destabilized, Fraction 4, A, water
- 35
- 40
- 45

Gas Evolution

		1997SW	Aldrich 50% HA	U4AW	U4A16	U4A22
5	2 mL Fe(III) 5000 ppm	1.97 mg	2.02	1.89 mg	2.16 mg	1.87 mg
	100 mL water or new stabilizer	102.4 mg H ₂ O	101.2 mg H ₂ O	101.6 mg H ₂ O	100.5 mg 16	99.5 mg 22
	1 mL HA	1221	1209.7	1195 mg	1200	1194
10	Vial	4.88 g	4.84 g	4.85	4.82	4.92
		0 6.06	0 5.99	0 5.98	0 5.94	0 6.09
		1 6.05 0.01 2 6.04 0.02	1 5.99 0 2 5.99 0	1 5.98 0 2 5.98 0	1 5.94 0 2 5.94 0	1 6.09 0 2 6.09 0
15		3 6.04 0.02 4 6.02 0.04	3 5.99 0 4 5.98 0.01	3 5.96 0.02 4 5.95 0.03	3 5.94 0 4 5.94 0	3 6.09 0 4 6.08 .01
		5 5.98 0.08 6 5.88 0.18	5 5.98 0.01 6 5.98 0.01	5 5.91 9.07 6 5.87 0.11	5 5.94 0 6 5.94 0	5 6.07 .02 6 6.07 .02
		7 5.82 0.24 8 5.29 0.27	7 5.97 0.02 8 5.95 0.04	7 5.86 0.12 8 5.85 0.13	7 5.94 0 8 5.94 0	7 6.07 .02 8 6.06 .03
20		9 10 5.78 0.28	9 5.95 0.04 10 5.94 0.05	9 5.84 0.14 10 5.84 0.14	9 5.94 0 10 5.94 0	9 6.06 .03 10 6.06 .03
			14 5.88 0.11 15 5.87 0.12	16 5.83 0.16	15 5.94 0	15 6.06 0.04
25		20 5.76 0.30	20 5.83 0.16	20 5.81 0.15	20 5.94 0	20 6.03 0.05

1997SW = 1997 stabilized + H₂O

Aldrich = Aldrich + H₂O

U4AW = 1997 destabilized Fraction 4, A = 1st, water

30 U4A16 = Ethylenebis(oxyethylenenitrilo)tetraacetic
99.4 mg / 10 mL H₂O 40991-0250

U4A22 = 1,4,8,11-Tetraazacyclotetradecane-5,7-dione
102 mg / 10 mL 33,316-6

35

40

45

8

Gas Evolution Testing of New Stabilizers

		1997SW	1997S28	1997S29	1997S14	1997S23	1997S4
5	2 mL Fe(II) 5000 ppm Fe	1.61 mg	1.76 mg	1.84 mg	1.92	1.97	2.00
	100 mL water or New Stabilizer	100.5 mg	100 mg 28	101.6 mg	97.2	101.9 23	96.3 4
	1 mL HA	1225	1220 mg	1221 mg	1221	1230	1222
10	Vial	4.85	4.81	4.87	4.85	4.91	4.85
	Time 0	6.06	5.98	6.06	6.06	0 6.14 0	6.07
	min 1	6.06 0	5.98	6.06	6.06 0	1 6.14 0	6.06 .01
	2	6.05 .01	5.97 .01	6.05 .01	6.07 -.01	2 6.14 0	6.06 .01
	3	6.04 .02	5.96 .02 B	6.05 .01 B	6.06 0	3 6.14 0	6.06 .01
15	4	6.04 .02	5.95 .03 B	6.03 .03	6.06 0	4 6.14 0	6.06 .01
	5	6.00 .06	5.89 .09 VB	6.00 .06 VB	6.06 0	5 6.14 0	6.06 .01
	6	5.91 .15	5.83 .15 VB	5.96 .10 VB	6.04 .02	6 6.14 0	6.06 .01
	7	5.81 .25	5.79 .19 B	5.94 .12 VB	6.04 .02	7 6.14 0	6.06 .01
	8	5.75 .31	5.77 .21 B	5.12 .14 B	6.03 .03	8 6.14 0	6.06 .01
	9	5.25 .31	5.76 .22	5.90 .16	6.01 .05	9 6.14 0	6.06 .01
20	10	5.75 .31		5.89 .17	6.00 .06	10 6.14 0	6.06 .01
	15	5.73 .33	5.75 .23	5.86 .20 11	5.93 .13	15 6.14 0	6.06 .01
	20	5.72 .34	5.75 .23	5.85 .21 12 13	5.89 .17 5.82 .24	20 6.14 0	6.06 .01
25	wt loss	0.34 g	0.23 g	0.21 g 14 15	5.78 .29 5.77 .29	wt loss = 0	wt loss = 0.01

1997SW = 1997 Stabilized + 100 mL H₂O

1997S28 = 1997 Stabilized + 100 mL Polystyrene

sulfononic acid-comaleicacid sodiumsalt 102.5 mg/10 mL

30 1997S29 = 1997 Stabilized + 100 mL Polyacrylic

acid sodium salt 40% 304.8 mg/10 mL

1997S14 = 1997 Stabilized + 100 mL 2,5-dihydroxy-

1,4-benzenediaceticacid 107.4 mg/10 mL

1997S23* = 1997 Stabilized + 100 mL CDTA 105 mg/10 mL H₂O

35 1997S4* = 1997 Stabilized + 100 mL FLUOREXON 101.3 mg/10 mL H₂O

* little or no wt loss : little or no decomposition

B = Bubbles

40 V = Vigorous

Gas Evolution

	U4A17	U4A21	U4A19	U4A23	1997S23	
5	2 mL Fe(III) 5000 ppm Fe ¹³	1.86 mg	1.90	1.90	1.25	1.80
	100 mL H ₂ O or New Stabilizer	100.9 mg 17	101.3 21	100.6 19	11.8 23 98.8 H ₂ O	11.4 mg 23 99.9 mg H ₂ O
10	1 mL HA	1191 mg	1194	1191	1189	1224
	Vial	4.96	4.93	4.85	4.84	4.85
15		0 6.08 1 6.07 0.01	0 6.10 1 6.10 0	0 6.01 1 6.01 0	0 6.01 1 6.01 0	0 6.05 1 6.05 0
		2 6.08 0 3 6.06 0.02	2 6.10 0 3 6.09 0.01	2 6.01 0 3 6.01 0	2 6.01 0 3 6.01 0	2 6.05 0 3 6.05 0
		4 6.04 0.04 5 6.02 0.06	4 6.08 0.02 5 6.05 0.05	4 6.01 0 5 6.01 0	4 6.01 0 5 6.01 0	4 6.05 0 5 6.05 0
		6 6.00 0.08 7 5.99 0.09	6 6.01 0.09 7 5.98 0.12	6 6.01 0 7 6.01 0	6 6.01 0 7 6.01 0	6 6.05 0 7 6.05 0
20		8 5.97 0.11 9 5.96 0.12	8 5.97 0.13 9 5.96 0.14	8 6.01 0 9 6.01 0	8 6.01 0 9 6.01 0	8 6.05 0 9 6.05 0
		10 5.95 0.13 15 5.94 0.14	10 5.95 0.15 15 5.94 0.16	10 6.01 0 15 6.01 0	10 6.01 0 15 6.01 0	10 6.05 0 15
		20 5.93 0.15	20 5.93 0.17	20 6.01 0	20	20 6.05 0

25

U4A17 U = unstabilized 1997, 4th Fraction,
A 1st, 17 N,N' dicarbocymethyl-
diaz-28-crown-6

99 mg/10 mL H₂O

U4A21 = Krypto Fix 222

106.4 mg/10 mL H₂O

30

U4A19 = Diethylenetriaminepentaacetic
acid 28,556-0

101.4 mg/10 mL

U4A23 = CDTA

105 mg/10 ml H₂O

35

40

45

10

	1997SW	U4AW	U4A26	U4A25	U4A24	U4A11	U4A14	
	2 mL Fe(III) 5000 ppm Fe ¹³	1.94	1.89	1.97	1.99	1.99	1.79	1.88
5	100 mL H ₂ O or New Stabilizer	100.6 mg	99.8	99.7 26	101	95.5 25	99.1 11	98.9 mg 14
	1 mL HA	1221 mg	1195	1188	1203	Green/ Yellow	1207 Amber	
	Vial	4.84	4.84	4.95	4.95	4.87	4.84	4.93
10	0	6.04	5.99	6.11	6.07	6.02	6.00 0	6.07
	1	6.04	5.99 0	6.11 0	6.07	6.02 0	6.00 0	6.07
	2	6.04	5.99 0	6.12 -.01	6.07	6.02 0	6.00 0	6.07
	3	6.03 .01	5.98 .01	6.11 0	6.07	6.02 0	6.00 0	6.06 .01
	4	6.02 .02	5.97 .02	6.11 0	6.07	6.02 0	6.00 0	6.06 .01
	5	5.97 .02	5.93 .06	6.11 0	6.07	6.02 0	6.00 0	6.05 .02
15	6	5.87 .17	5.91 .08	6.11 0	6.06 .01	6.02 0	5.99 .01	6.05 .02
	7	5.80 .24	5.89 .10	6.11 0	6.06 .01	6.02 0	6.00 .01	6.04 .03
	8	5.78 .26	5.87 .12	6.11 0	6.06 .01	6.02 0	6.00 0	6.03 .04
	9	5.77 .27	5.86 .13	6.12 -.01	6.05 .02	6.02 0	6.00 0	6.02 .05
	10	5.76 .28	5.86 .13	6.11 0	6.05 .02	6.02 0	6.00 0	6.01 .06
	15	5.75 .29	5.83 .16	6.11 0	6.04 .03	6.02 0	5.99 .01	5.98 .09
20	20	5.75 .29	5.83 .16	6.12 -.01	6.04 .03	6.02 0	5.99 .01	5.97 .10

1997SW 1997 stabilized water

U4AW 1997 destabilized + water

25 U4A26* 1997 destabilized + triethylenetetraamine,
N,N,N',N'',N''',N''' hexaacetic acid 105.6 mg/10 mL

U4A25 1997 destabilized + inositol hexa-
phosphoric acid 40-50% 187 mg/10 mL

30 U4A24* 4,8 dihydroxyguinoline-2-carboxylic
acid 99.6 mg/10 mL

U4A11* 4,7 dihydroxy-1,10-phenanthroline 51.3 mg/10 mL

UA414 2,5 dihydroxy-1,4-benzenediacetic
acid 107.4 mg/10 mL

35

40

45

11

General Titration Procedure

Determination of remaining NH_2OH after gas evolution Test: General Procedure: First wash contents of 10 mL plastic beaker with 2 mL conc HCl + 5 mL H_2O , transfer HCl + washings to 200 mL Volumetric Flask. After completion of the gas evolution experiment, transfer contents of 4 mL Vial to 200 mL Volumetric Flask. Add 2 mL HCl to Vial wash with 10-20 mL H_2O , Transfer all washings to 200 mL volumetric Flask. Dilute up to Volume. Take 10 mL aliquot and titrate with 0.25 N NaOH.

From page 27

calculation for HA = Hydroxylamine

1 mL = $\cong$ 1.1 g

$$\text{mL} \times \frac{.25 \text{ mole}}{1000 \text{ mL}} \times \frac{1}{1.1 \text{ g}} \times \frac{33 \text{ g}}{\text{mole}} \times \frac{200 \text{ mL}}{10 \text{ mL}} \times 100 = \% \text{ HA or mL} \times 15$$

15

1997SW = 1 mL 1997 Stabilized + 100 mL H_2O + 2 mL Fe^{+3} (5000 ppm)

	HCl	6.761	}	1.095 mL x 15 = 16% HA
20	NH_3OH	7.856		
	NH_4	8.139	}	1.283 mL $\times \frac{.25 \text{ mole}}{1000 \text{ mL}} \times \frac{1}{1.1 \text{ g}} \times \frac{17 \text{ g}}{\text{m}} \times \frac{200}{10} \times 100 = \% \text{ NH}_3 \text{ or } 7.7$

↙ 2.2% NH_3

25 1997S28 = 1mL 1997 Stabilized + 100 mL Polystyrenesulfonate-co-maleic acid, sodium salt + 2 mL (Fe^{+3} 5000 ppm)

	HCl	5.694	}	1.494 mL x 15 = 22% HA
	NH_3OH	7.188		
30	NH_4	7.535		0.347 x 7.7 = 2.7% NH_3

35

40

45

12

1997S29 = 1 mL 1997 stabilized + 100 mL of $\approx$ 10000 ppm polyacrylic acid sodium salt
40% 304.8 mg/10 mL + 2 mL of Fe(III) 5000 ppm

5 HCl 4.436 mL $\begin{matrix} \searrow 2-1 \\ \nearrow 3-2 \end{matrix}$ 1.193 mL x 13 = 17.9% HA
NH₃OH 5.629 mL
NH₄ 6.192 mL 0.563 mL x 27 = 4.3% NH₃

10 1997S14 = 1 mL 1997 stabilized + 100 mL of 2,5 dihydroxy-1,4-benzenediacetic acid
107.4 mg/10 mL, + 2 mL of Fe(III) 5000 ppm

15 HCl 7.022 $\begin{matrix} \searrow 2-1 \\ \nearrow 3-2 \end{matrix}$ 0.813 mL x 15 = 12.2% HA
NH₃OH 7.835
NH₄ 1.162 0.327 mL x 7.7 = 2.52% NH₃

1997S23 = 1 mL 1997 stabilized + 100 mL of CDTA 105 mg/10 mL, 2 mL of Fe(III) 5000 ppm

20 HCl 3.541 $\begin{matrix} \searrow \\ \nearrow \end{matrix}$ 3.683 mL x 15 = 55.2% HA
NH₃OH 7.224
NH₄ NO NH₃

25 1997S4 = 1 mL 1997 stabilized + 100 mL of Fluorexon (11,985-7 Cat# Aldrich)
101.3 mg/10 mL + 2 mL of Fe(III) 5000 ppm

HCL 3.565 $\begin{matrix} \searrow \\ \nearrow \end{matrix}$ = 3.581 mL x 13 = 53.7% HA
NH₃OH 7.146

30 HA = hydroxyl amine Note 1997S23 + 19974 showed little or no decomposition

35

40

45

13

Gas Evolution

	2 mL Fe(III) 500 ppm	1997S32 1.97 mg	1997S31 1.93 mg
5	100 mL H ₂ O or New Stabilizer	101 mg	101.3 mg
	1 mL of 1997S Σ	1218 mg	1222 mg
	Vial empty	4.93 g	4.89
		0 6.10 1 6.09	0 6.09 1 6.09
10		2 6.10 3 6.08 B	2 6.09 B 3 6.08
		4 6.08 B 5 6.05 VB	4 6.06 VB 5 6.03 VB
		6 6.02 VB 7 6.00 VB	6 5.93 7 5.83 VB
15		8 5.98 9 5.97	8 5.77 VB 9 5.75
		10 5.95 15 5.91	10 5.74 15 5.73
		20 5.89	20 5.72
20		wt loss 0.21 g	wt loss 0.37
	1997S32 = 1 mL 1997S 113 mg/10 mL 1,2bis(2 amino phenoxy) ethane N,N,N',N' tetracetic acid		1997S31 = 1 mL 1997S 100 ml of Trans-Aconitric acid 105 mg/10 mL

25

HCL 6.810 > 1.159 mL x 15 = 17.4% HA
 NH₃OH 7.969 >
 NH₄ 8.577 > 0.602 mL x 7.7 = 4.7% NH₃

HCL 7.336 > 0.84 x 15 = 12.6% HA
 NH₃OH 8.176 >
 NH₄ 8.466 > 0.29 x 7.7 = 2.2% NH₃

30

B = Bubbles
 V = Vigorous

35

40

45

Gas Evolution + Titration

Sample	1997S34	1997S35	HA = Hydroxylamine
2 mL Fe(III) 5000 ppm	1.98 mg	1.98 mg	
100 mL New Stabilizer	101 mg	102.5 mg	
1 mL 1997S Σ	1229 mg	Σ 1225 mg	
Vial empty	4.90 g	4.82 g	
	Time Min	Time Min	
	0 6.12	0 6.05	
	1 6.12	1 6.05	
	2 6.11	2 6.05	
	3 6.10 B	3 6.05	
	4 6.09	4 6.05	
	5 6.04 VB	5 6.05	
	6 5.92	6 6.05	Note 1997S35 little or NO wt loss in little or NO HA decomposition
	7 5.84 VB	7 6.05	
	8 5.82	8 6.04 B	
	9 5.81	9 6.04	
	10 5.80	10 6.05	
	15 5.79	15 6.04	
	20 5.79	20 6.03	
	wt loss 0.33 g	wt loss 0.02 g	
1 mL 1997S 100 mL 34 = 1,1'-Ethylenebis(5-oxo-3-pyrrolidine carboxylic acid Cat# 32, 756-S Ainch		1 mL 1997S 100 mL 109 mg 2,3 dihydroxybenzoic acid	

HCl 6.930 $\begin{matrix} > \\ > \end{matrix}$ 1.153 mL x 15 = 15.8% HA
 30 NH₃OH 7.983 $\begin{matrix} > \\ > \end{matrix}$ 0.322 mL x 7.7 = 2.47% NH₃
 NH₄ 8.305

HCL 5.042 $\begin{matrix} > \\ > \end{matrix}$ 3.306 mL x 15 = 49.6% HA
 NH₃OH 8.348 $\begin{matrix} > \\ > \end{matrix}$ 0.203 mL x 7.7 = 1.56% NH₃
 NH_Y 8.331

B = Bubbles

35 V = Vigorous

slight Color, Note splash

of Vial contents on addition of HCl

40

45

15

Gas Evolution + Titration

	sample	1997S33	1997S19	1997S36	1997S40	1997S26
5	5000 ppm Fe 2 mL	2.17 mg	2.43 mg	2.09 mg	2.11 mg	1.98 mg
	100 mL New Stabilizer Σ	101.8 mg	Σ 101.6 mg	100.8 mg	101 mg	100 mg
	1 mL 1997S Σ	1225 mg	Σ 1224 mg	Σ 1220 mg	1220 mg	1220 mg
10	Vial empty	4.93 g	4.88 g	4.88 g	4.82 g	4.85 g
	Time Minutes					
	0	6.13 g	6.09 g	6.10 g	5.95 g	6.07 g
	1	6.13 g	6.10 g	6.10 g	5.95 g	6.07 g
	2	6.13 g	6.10 g	6.10 g	5.95 g	6.07 g
15	3	6.12 g B	6.10 g	6.10 g	5.94 g	6.07 g
	4	6.10 g	6.10 g	6.10 g	5.92 g VB	6.07 g
	5	6.03 g VB	6.10 g	6.10 g	5.89 g VB	6.07 g
	6	5.93 g VB	6.10 g	6.10 g	5.83 g VB	6.07 g
20	7	5.88 g VB	6.10 g	6.10 g	5.78 g VB	6.07 g
	8	5.86 g	6.10 g	6.10 g	5.75 g	6.07 g
	9	5.85 g	6.10 g	6.10 g	5.73 g	6.07 g
	10	5.85 g	6.10 g	6.10 g	5.73 g	6.07 g
	15	5.84 g	6.09 g	6.10 g	5.71 g	6.07 g
25	20	5.84 g	6.10 g	6.10 g	5.70 g	6.07 g
		wt loss 0.29 g	wt loss 0 g	wt loss 0 g	wt loss 0.25 g	wt loss 0 g

30 1997S33 = 1 mL 1997S + 100 mL 2,2'-(Ethylenedithio)diacetic acid
103 mg / 10 mL, 2 mL of 5000 ppm Fe

35 $\begin{matrix} \text{HCl} & 4.936 \\ + \\ \text{NH}_3\text{OH} & 6.115 \\ + \\ \text{NH}_4 & 6.441 \end{matrix} \begin{matrix} > \\ > \end{matrix} \begin{matrix} 1.179 \text{ mL} \times 15 = 17.7\% \text{ HA} \\ 0.326 \text{ mL} \times 7.7 = 2.5\% \text{ NH}_3 \end{matrix}$

40 Note 1997S19, 1997S36 + 1997S26 showed little or no wt loss in
little or no decomposition

16

Gas Evolution + Titration

1997S19 = 1 mL 1997 Stabilized, 100 mL of Diethylene triamine
pentaacetic acid (28,556-0 cat# Aldrich) 101.4 mg / 10 mL, 2 mL of 5000 ppm Fe

5

HCl	4.800	>	3.734 mL x 15 = 56.0% HA = hydroxyl amine Note Little or no Decomposition of 1997S
NH ₃ OH	8.534		
NH ₄	None	>	

10

1997S36 = 1 mL 1997 Stabilized, 100 mL of N,N'-Bis(2-carboxyethyl)-N,N' ethylenediglycine
trihydrate (Aldrich 28,584-6)

15

HCl	4.769	>	3.634 mL x 15 = 54.5% HA Note Little or no Decomposition of 1997S
+			
NH ₃ OH	8.403	>	
+			
NH ₄	None		

20

1997S40 = 1 mL 1997 stabilized, 100 mL 1,2,3,4 Butanetetracarboxylic acid 105.9 mg / 10 mL,
2 mL of 5000 ppm Fe

HCl	6.367	>	1.253 x 15 = 18.8% HA
NH ₃ OH	7.620		
NH ₄	8.014	>	0.394 x 7.7 = 3% NH ₄ ⁺

25

1997S26 = 1 mL 1997 Stabilized, 100 mL Triethylenetetramine N,N,N,N, hexaacetic acid

30

HCl	4.928	>	= 3.633 mL x 15 = 54.5% HA
+			
NH ₃ OH	8.561	>	no NH ₃ Little or no Decomposition of 1997S
+			
NH ₄			

35

40

45

17

Gas Evolution + Titration

	sample	1997S9	1997S13	1997S16	1997S22	1997S24	1997S11	1997S25
5	5000 ppm Fe 2 mL	1.72 mg	2.07	1.70	2.02	1.89	1.76	2
	New Stabilizer 100 mL	Σ 101.4 mg	Green 101.9 Color	101.2	100	Greenish 99.7 Color	Redish 98.4	99
	1997S H-Base 55% HA 1 mL	Σ 1220 mg	Rose 1221 Color	1220	1222	Yellow 1218	1215	1224
10	Vial Empty	4.86	4.90	4.83	4.89	4.85	4.95	4.83
	Time (Min.)							
	0	6.05	6.12	6.07	6.10	6.04	6.11	6.07
	1	6.05	6.12	6.07	6.10	6.04	6.11	6.07
	2	6.05	6.12	6.07	6.09	6.04	6.11	6.07
15	3	6.05	6.12	6.07	6.08 B	6.04	6.11	6.07
	4	6.05	6.12	6.07	6.08	6.04	6.11	6.08
	5	6.05	6.12	6.07	6.07	6.04	6.11	6.07
	6	6.05	6.12	6.07	6.07	6.04	6.11	6.07
20	7	6.05	6.12	6.07	6.06	6.04	6.11	6.05
	8	6.05	6.12	6.07	6.06	6.04	6.11	6.04
	9	6.05	6.12	6.07	6.06	6.04	6.11	6.04
	10	6.05	6.12	6.07	6.05	6.04	6.11	6.03
	15	6.05	6.12	6.07	6.04	6.04	6.11	5.98
25	20	6.05	6.12	6.07	6.04	6.04	6.10	5.95
	wt loss	0	0	0	.06 mg	0	.01	0.12 g

	sample	1997S13	0	6.06
30	5000 ppm		1	6.06
	2 mL Fe	2.00	2	6.06
	New		3	6.06
	Stabilizer	100.3	4	6.05
	1997S		5	6.05
35	HB	1220	6	5.92
			7	5.82
	Vial	4.87	8	5.80
			9	5.79
			10	5.79
40			15	5.79
			20	5.79

45

18

1997S9 = 1 mL 1997 Stabilized HBase 55% HA, 100 mL of 1,4,8,11 Tetraazacyclotetradecane-1,4,8,11-tetracetic acid (Aldrich 40,040-8)
100.9 mg / 10 mL H₂O, 2 mL of 5000 ppm Fe(III)

5 HCl 4.436 mL
+
NH₃OH 7.916 8.020 mL
+
NH₄ 8.02

> 3.584 mL x 15 = 53.8% HA

↗

10 1997S13 = 1 mL 1997 Stabilized HB 55% HA, 100 mL of 4,5 Dihydroxy-1,3-benzene disulfonic Acid, disodiumsalt (Aldrich 17,255-3) 106.3 mg/10 mL H₂O, 2 mL 5000 ppm Fe(III)

HCl 6.391 mL
+
NH₃OH 10.009 mL

> = 3.618 mL x 15 = 54% HA

15

1997S16 = 1 mL 1997 Stabilized HB 55% HA, 100 mL of Ethylene bis(oxyethylenetriolo)-tetraacetic acie (40991-0250)
99.4 mg/10 mg H₂O, 2 mL of 5000 ppm Fe(III)

20 HCl 4.437
+
NH₃OH 7.933
+
NH₄ None

> 3.496 x 15 = 52.4%

25 1997S22 = 1 mL 1997 Stabilized HBase 55% HA, 100 mL of 1,4,8,11-tetraazacycloetradecane-5,7-dione (33.316-6 cat#) 102 mg/10 mL, 2 mL of 5000 ppm Fe

30 HCl 4.781
+
NH₃OH 7.554
+
NH₄ 7.966

> 2.773 x 15 = 41.6% HA

> 0.412 x 7.7 = 3.2% NH₄

35

40

45

19

1997S24 = 1 mL 1997 Stabilized HBase 55% HA, 100 mL of 4,8-Dihydroxy quinoline-2-carboxylic acid 99.6 mg/10 mL, 2 mL of 5000 ppm Fe

$$\begin{array}{lcl} \text{HCl} & 4.176 \text{ mL} & \\ + & & \\ \text{NH}_3\text{OH} & 7.787 \text{ mL} & \end{array} \begin{array}{l} > \\ > \end{array} \begin{array}{l} = 3.611 \times 15 = 54.2\% \text{ HA} \end{array}$$

1997S11 = 1 mL 1997 Stabilized HBase 55% HA, 100 mL of 4,7 dihydroxy 1,10 phenanthroline 51.3 mg/10 mL, 2 mL of 5000 ppm Fe(III)

$$\begin{array}{lcl} \text{HCL} & 5.080 & \\ & & \\ \text{NH}_3\text{OH} & 8.469 & \\ & & \\ \text{NH}_4 & 8.619 & \end{array} \begin{array}{l} > \\ > \end{array} \begin{array}{l} = 3.389 \times 15 = 50.8 \text{ HA NH}_2\text{OH} \\ = .149 \times 7.7 = 1.1 \text{ NH}_3 \end{array}$$

1997S25 = 1 mL 1997 Stabilized HBase 55% HA, 100 mL of Inositol hexaphosphoric acid (40-50% Sol'n) 187 mg/10 mL, 2 mL of 5000 ppm Fe

$$\begin{array}{lcl} \text{HCL} & 5.716 & \\ & & \\ \text{NH}_3\text{OH} & 7.593 & \\ + & & \\ \text{NH}_4 & 8.243 & \end{array} \begin{array}{l} > \\ > \end{array} \begin{array}{l} 1.877 \times 15 = 28.2\% \text{ HA NH}_2\text{OH} \\ 0.652 \times 7.7 = 5.0\% \text{ NH}_3 \end{array}$$

1997S15 = 1 mL 1997 Stabilized HBase 55% HA, 100 mL of 1,4,10,13-tetroxa-7,16-diazacyclooctadecane (29,580-9 Aldrich) 104.3 mg/10 mL H₂O, 2 mL of 5000 ppm Fe

$$\begin{array}{lcl} \text{HCL} & 6.985 & \\ - & & \\ \text{NH}_3\text{OH} & 8.173 & \\ + & & \\ \text{NH}_4 & 8.523 & \end{array} \begin{array}{l} > \\ > \end{array} \begin{array}{l} 1.188 \text{ mL} \times 15 = 17.8\% \text{ HA} \\ 0.35 \text{ mL} \times 7.7 = 2.7\% \text{ NH}_4 \end{array}$$

30

35

40

45

20

Gas Evolution + Titration of new stabilizer

	sample	1997S41	1997S42	1997S39	1997S38	1997S37
5	5000 ppm Fe 2 mL	1.94 mg	2.09 mg	1.70 mg	2.07 mg	2.22 mg
	New Stabilizer 100 mL	Σ 1023 mg	97.7 mg	100.4 mg red	100 mg Green	100 mg
	1997S 56% HA 1 mL	Σ 1224 mg	1221 mg	light 1238 mg yellow	light 1224 mg orange	1238 mg
10	empty Vial	4.85 g	4.87 g	4.95 g	4.82 g	4.88 g
	Time (Min.)					
	0	6.06	6.08	6.17	6.05	6.11
	1	6.06	6.08	6.17	6.05	6.11
	2	6.06	6.08	6.17	6.05	6.11
15	3	6.06	6.08	6.16	6.05	6.11
	4	6.04	6.08	6.14	6.05	6.11
	5	6.03	6.07	6.11	6.05	6.11
	6	5.98	6.07	6.05	6.05	6.11
20	7	5.88	6.07	5.99	6.05	6.11
	8	5.82	6.06	5.95	6.05	6.11
	9	5.78	6.06	5.94	6.05	6.11
	10	5.76	6.06	5.93	6.05	6.11
	15	5.75	6.05	5.92	6.05	6.11
25	20	5.74	6.04	5.91	6.05	6.11
	wt loss	0.32 g	0.04 g	0.26 g	0 mg	0 g

30

1997S41 = 1 mL 1997 Stabilized HBase 56% HA, 100 mL of (+)-Cis-Epoxytricarbollic acid
100 mg/10 mL, 2 mL of 5000 ppm Fe(III)

vial + 3/4 mL HCl → 200 mL, 10 mL aliquot

35 HCL 6.622 mL
+
NH₃OH 7.530
+
NH₄ 7.876

> 0.908 mL x 15 = 13.6% HA

> 0.346 mL x 7.7 = 2.66% NH₃

1997S42 = 1 mL 1997 Stabilized HBase 56% HA, 100 mL of N-(2-Acetamidaminodiacetic acid
105 mg/10 mL, 2 mL of 5000 ppm Fe(III)

40

HCL 5.209
+
NH₃OH 8.160
+
NH₄ 8.563

2.951 mL x 15 = 44.3% HA NH₂OH

0.403 mL x 7.7 = 3.1% NH₃

45

21

1997S39 = 1 mL 1997S Stabilized 56% HA, 100 mL of Salicylic Acid
7.8 mg/10 mL, 2 mL of Fe(III) 5000 ppm

$$\begin{array}{rcl}
 \text{HCl} & 6.800 & \\
 + & & \\
 \text{NH}_3\text{OH} & 8.015 & \\
 + & & \\
 \text{NH}_4 & 8.458 &
 \end{array}
 \begin{array}{l}
 > 1.215 \text{ mL} \times 15 = 18.2\% \text{ HA} \\
 > 0.443 \text{ mL} \times 7.7 = 3.4 \text{ NH}_3
 \end{array}$$

1997S38 = 1 mL 1997S Stabilized 56% HA, 100 mL of Thiosalicylic acid
101.6 mg/10 mL, 2 mL of 5000 ppm Fe(III)

10

$$\begin{array}{rcl}
 \text{HCl} & 4.377 & \\
 + & & \\
 \text{NH}_3\text{OH} & 7.942 & \\
 + & & \\
 \text{NH}_4 & 0 &
 \end{array}
 \begin{array}{l}
 > 3.565 \text{ mL} \times 15 = 5.3\% \text{ HA}
 \end{array}$$

15

1997S37 = 1 mL 1997S Stabilized 56% HA, 100 mL of CDTA
112 mg/10 mL, 2 mL of 5000 ppm Fe(III)

$$\begin{array}{rcl}
 \text{HCl} & 2.713 & \\
 + & & \\
 \text{NH}_3\text{OH} & 6.390 &
 \end{array}
 \begin{array}{l}
 > 3.677 \text{ mL} \times 15 = 55\% \text{ HA}
 \end{array}$$

20

25

30

35

40

45

New stabilizer screening
Gas evolution + titration

sample		1997S43	1997S45	1007S46
5	2 mL 500 ppm Fe(III)	1.80 mg	100 mg	1.93
	new stabilizer 100 mL	100 mg	100 mg	100.7
	1997S H-base 56% Hydroxylamine	1223 mg	1229 mg	1232
	Vial	min	4.83 g	4.91 g
10		0	6.06	6.11
		1	6.06	6.11
	Note: After wt loss content	2	6.06	6.12
	of vial transferred to 200 mL	3	6.05	6.12
	Volumetric Flask, 3-4 mL	4	6.04	6.12
15		5	6.02	6.12
	Conc HCl Aldrich, diluted	6	6.00	6.12
		7	5.98	6.12
	to volume, 10 mL aliquot	8	5.95	6.12
20	titrated using 0.25 NaOH	9	5.93	6.12
		10	5.91	6.12
		15	5.88	6.12
		20	5.86	6.12
	wt loss		0.20 g	0 g

25

1997S43 = 1 mL 1997S 56% HA, 100 mL of 2-Carboxyethylphosphonic acid,
2 mL of 5000 ppm Fe(III) 99 mg/10 mL

30 HCl 3.660 mL
+ 1.254 mL x 15 = 18.8% HA
NH₃OH 4.914 mL
+ 0.612 mL x 7.7 = 4.7% NH₃
NH₄ 5.526 mL

35 1997S45 = 1 mL 1997S 56% HA, 100 mL of Mercaptonicotinic Acid
97.9 mg/10 mL, 2 mL of 5000 ppm Fe(III)

40 HCl 2.704
+ 3.61 mL x 15 = 54% HA
NH₃OH 6.314
+
NH₄ 0

1997S46 = 1 mL 1997S 56% HA, 100 mL of cyxtime 96 mg/10 mL
2 mL of 5000 ppm Fe(III)

45 HCl 2.767
+ 3.465 x 15 = 52% HA
NH₃OH 6.232
+ 0.147 x 7.7 = 1.1% NH₃
NH₄ 6.379

I CLAIM:

1. A stabilized hydroxylamine solution comprising a stabilizer
5 selected from the group consisting of (a) 1,4,8,11-tetraaza-
cyclotetradecane-1,4,8-11-tetraacetic acid, (b) 4,8-dihydro-
xyquinoline-2-carboxylic acid, (c) 4,5-dihydroxy-1,3-benzene-
disulfonic acid, (d) 4,7-dihydroxy-1,10-phenanthroline,
10 (e) 2-mercaptonicotinic acid (f) bis[N,N-bis(carboxy-
methyl)-aminomethyl]fluorescein, (g) N,N'-bis(2-carboxy-
ethyl)-N,N'-ethylenediglycine trihydrate, (h) cystine,
(i) 2,3-dihydroxybenzoic acid, (j) thiosalicylic acid and
(k) any mixture of the foregoing.
- 15 2. The stabilized solution as defined in claim 1 wherein said
stabilizer is present in said solution in an amount ranging
from 0.005 percent to 0.1 percent by weight to the total
weight of the stabilized solution.
- 20 3. A method of stabilizing a hydroxylamine solution which
comprises adding a stabilizer to the solution wherein said
stabilizer is selected from the group consisting of (a)
1,4,8,11-tetraazacyclotetradecane-1,4,8-11-tetraacetic acid,
25 (b) 4,8-dihydroxyquinoline-2-carboxylic acid,
(c) 4,5-dihydroxy-1,3-benzenedisulfonic acid, (d) 4,7-di-
hydroxy-1,10-phenanthroline, (e) 2-mercaptonicotinic acid,
(f) bis[N,N-bis(carboxymethyl)-aminomethyl]fluorescein,
(g) N,N-bis(2-carboxyethyl)-N,N'-ethylenediglycine trihydrate,
(h) cystine, (i) 2,3-dihydroxybenzoic acid, (j) thiosalicylic
30 acid and (k) any mixture of the foregoing.
4. The method as defined in claim 3 wherein said stabilizer is
added to yield an amount thereof in the solution of 0.005
percent to 0.1 percent by weight to the total weight of the
35 solution.

40

45