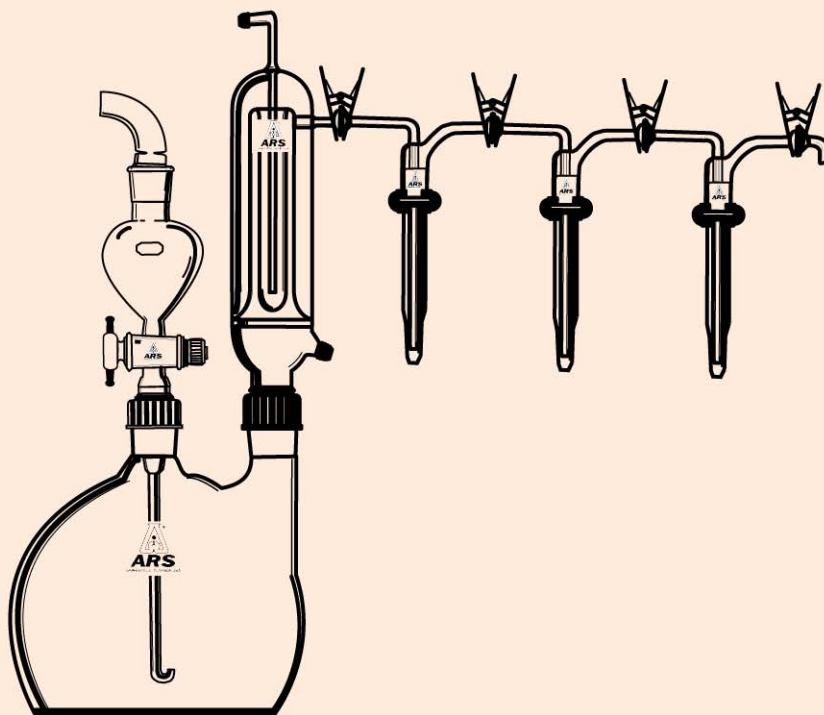




ANALYTICAL RESEARCH SYSTEMS, Inc.

"Serving the Scientific & Engineering needs of Government, Academia, & Industry"

Carbon Disulfide Evolution Apparatus

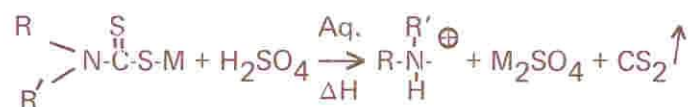


DESIGNED FOR DETERMINATION OF
THIO- AND DITHIOCARBAMATES

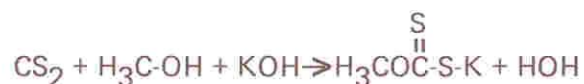
Bulletin CS-780

DETERMINATION OF THIO- AND DITHIOCARBAMATES USING THE SSI CARBON DISULFIDE EVOLUTION APPARATUS

Dithiocarbamates are determined indirectly by converting them to xanthates. The first step is the decomposition of dithiocarbamate to carbon disulfide according to the equation:



where R and R' may be alkyl, aryl, or hydrogen (1, 2). The carbon disulfide is then converted to an alkyl xanthate (usually methyl or ethyl).



which is optically determined at 380 nm (for the methyl xanthate in 0.5N KOH methanolic in H₃C-OH).

The method is non-specific and selective only for those compounds containing the $\overset{\text{S}}{\parallel}{\text{C}}-\text{S}$ moiety. This group includes salts of dithiocarbamic acids, dimers of the acids (thiuram disulfides) and other compounds.

The Knorr Alkalimeter is currently the apparatus most often used for determining dithiocarbamate in wastewater. However, the apparatus is fragile, difficult to clean, and allows excessive amounts of water and acid vapors to be swept over into the traps. This changes the trap solution resulting in unpredictable shifts of λ_{max} . An improved carbon disulfide evolution apparatus has therefore been developed.

The SSI Carbon Disulfide Evolution Apparatus permits analysis of larger aqueous samples by use of a one liter two-neck flat bottom acid digestion flask. The center neck (19/22) admits the addition funnel/dust trap assembly. The side neck (28/15 ball) is fitted to a high-efficiency condenser. By having the ball joint on the flask and the socket on the condenser, grease contamination into the flask is minimized.

The traps are miniaturized to increase the concentration of carbon disulfide with a resultant improvement in the detection limit. The trap train is assembled via 12/5 ball-socket ground glass joints for ease of assembly and disassembly. To complete the assembly, a larger trap reservoir containing 10% aqueous lead acetate is placed in the system before the miniature trap train for removal of acid fumes. The trap train is terminated via 12/5 socket adapter for hose connection to an aspirator.

GENERAL PROCEDURE

An improved procedure allows determination of individual salts of dithiocarbamic acids. An extraction with chloroform or methylene chloride removes the dimers of the acids (thiuram disulfides). These compounds are determined separately. The extracted sample is then charged into the SSI digestion flask. The addition funnel assembly and the condenser/trap assembly are attached to the flask. The trap receivers are charged with 0.5N KOH in Methanol. The aspirator and ballast flask are attached, the aspirator is started and the bubble rate in the trap flask is adjusted to be between 50 and 60 bubbles per minute.

Heating, cooling water, and magnetic stirring are started, and 25ml of 50% Aqueous H_2SO_4 are added. The reaction is allowed to proceed at the boil for 15 to 20 minutes. The bubble rate is maintained.

After 20 minutes, the mixture in the boiling flask is allowed to cool slightly, and the traps are removed. The xanthate solutions are combined and their volume is adjusted. The determination of the methyl xanthate is carried out at 380nm against a 0.5N KOH in H_3COH blank.

Another set of traps is charged with 10% HOAc and the traps are put in place. The solution in the boiling flask is made strongly alkaline with 50% Aqueous KOH and the distillation procedure is repeated.

The amines thus distilled are trapped as the acetates and can be determined by HPLC or by GC after appropriate treatment.

The contents of the boiling flask are then analyzed for the appropriate metals. The data are then compared with the Table of Composition to identify the compound or compounds. Table I is the table of compositions. Figure 1 shows the analytical sequence.

The SSI CS_2 Evolution Apparatus is the subject of a patent application, and was suggested for use in this type of analysis by U.S. EPA in RFP CI 80-0259.

LITERATURE CITED

1. Official Methods of Analysis. Association of Official Analytical Chemists, Washington, D.C.; 1980.
2. Spot Tests in Inorganic Analysis. Elsevier Publishing Co., New York, New York, 1958.

TABLE I. COMPOSITION OF CERTAIN DITHIOCARBAMATES

COMPOUND NAME	PARENT AMINE	MOLE METAL	RATIO	COMMENTS
Busan 40	Methoxy methylamine	Potassium	1:1:1	2
Busan 85	Dimethylamine	Potassium	1:1:1	2
Ferbam	Dimethylamine	Iron	1:3:1	3,8
KN Methyl	Methylamine	Potassium	1:1:1	2
Amobam	Ethylene diamine	Ammonia	2:1:2	2
Mancozeb	Ethylene diamine	Manganese/Zinc	1:1:2:4	3, 4, 5, 9
Manganous Benzothiazyl dithiocarbamate	2 amino-benzothiazole	Manganese	1:2:2	3, 9
Manganous Benzothiazyl-2-mercaptide	o-Toluidine	Manganese	1:2:2	3, 9
MBTS	o-Toluidine	None	0:2:2	6, 8
2-MBT	o-Toluidine	None	0:1:1	6, 8
Nabam	Ethylene diamine	Sodium	2:1:2	2
Polyram	Ethylene diamine	Zinc	1:2:4	3, 5, 9
Sodium dimethyl dithiocarbamate	Dimethylamine	Sodium	1:1:1	2
Sulfallate	Diethylamine	2-Chloropropene	1:1:1	7
Thiram	Dimethylamine	None	0:2:2	6, 8
Vancide PA	see Ferbam			
Zineb	Ethylene diamine	Zinc	1:2:1	3, 9

1) Metal: amine: CS₂

2) compound soluble in aqueous base

3) compound water-insoluble

4) Metal: metal: amine: CS₂

5) as the dimer

6) no metals associated

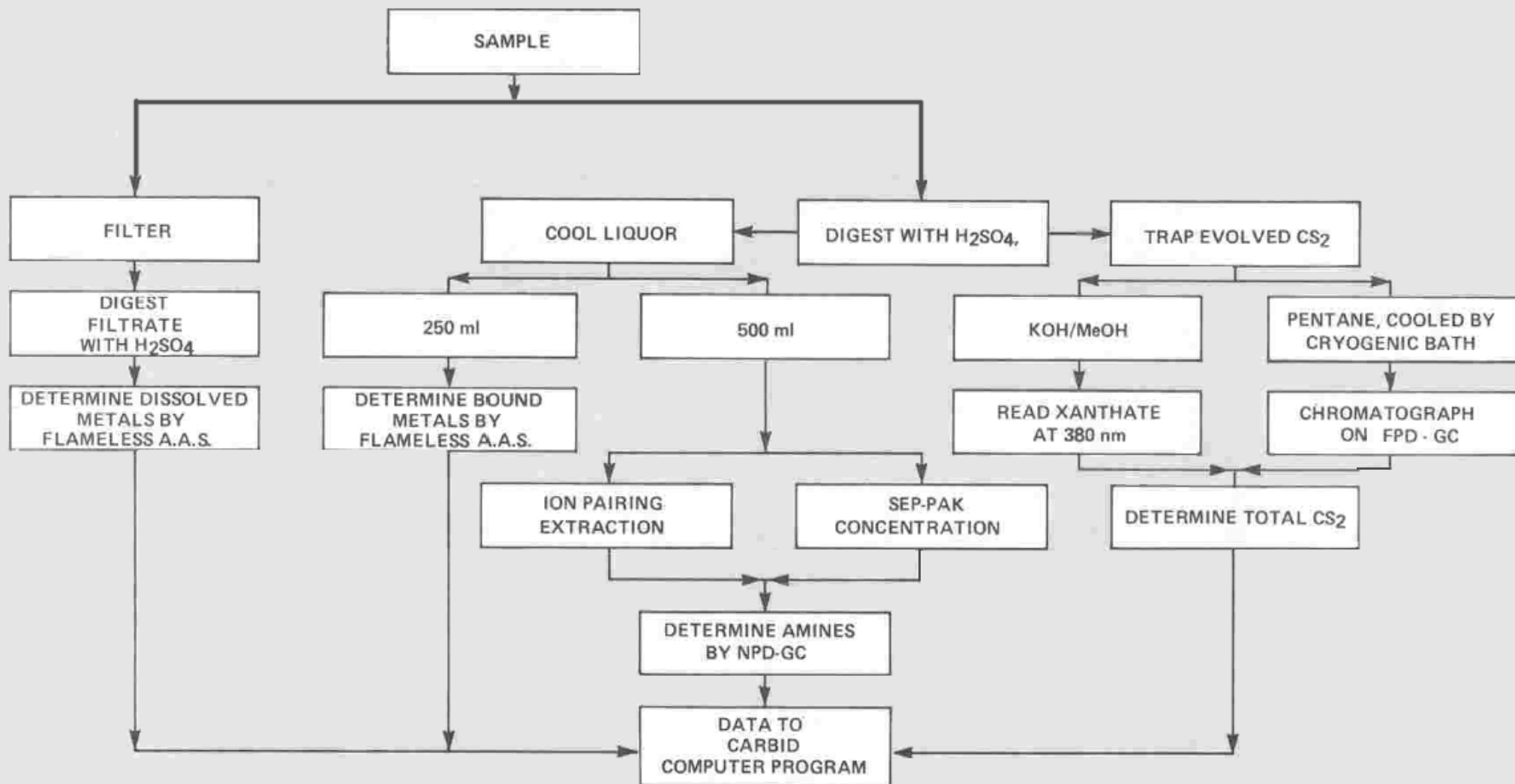
7) organic substituent

8) compound soluble in chloroform

9) may be dissolved by chelation with tetrasodium EDTA

DECOMPOSITION METHOD FOR DITHIOCARBONATES

(AFTER McCOWN, STROHSCHHEIN, HUCKS, and BAKER)



C D E A COMPONENTS



EAS-CDEA-010

19/22 I inlet dust trap
for packing glass wool.

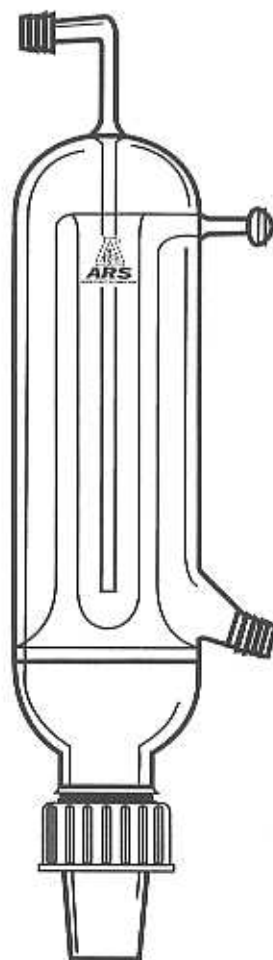


ENV-CDEA-020

50 ml acid addition funnel
with TFE stopcock & 19/22
I RV joint.

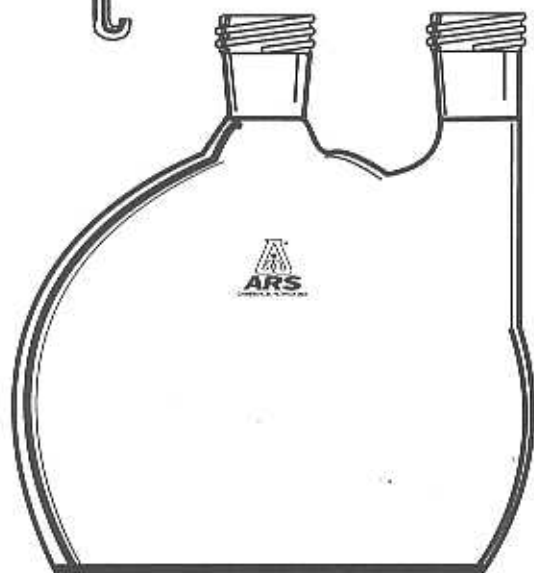
EAS-CDEA-100

M&S water-jacketed condenser
with 19/22 I RV inlet & 12/5 BJ
outlet.



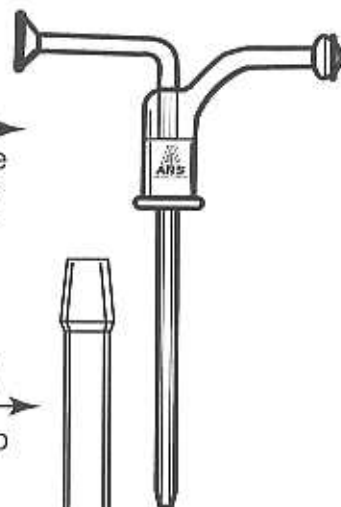
EAS-CDEA-210

1.5L Acid digestion flask
with 19/22 O RV necks.



EAS-CDEA-070

Standard 19/22 miniature
inlet trap with 12/5 o-ring
ball and 12/5 socket.



EAS-CDEA-050

Standard 19/22 trap
with receiver tip.



CLAMP-KCK-19

Size #19 Keck plastic retaining
clip for 19/22 joints on reciver
trap.



CLAMP-SS-P12

Size #12 (for 12/5 B&S Joints)
stainless steel pinch clamp.

