3920 © *1982 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* *55,* *3920—3922 (1982)* [Vol. 55, No. 12

Studies on the Concentrated Steffen Fluid of Beet Sugar Industry. I. On the Salt Separated from Concentrated Steffen Fluid Using Methanol and Sulfuric Acid

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(Received September 7, 1982)

The chemical desalting technique was applied to the concentrated Steffen fluid using concd sulfuric acid and methanol. The chemical components of the isolated salt were studied by scanning electron microscopy, infrared spectroscopy, X-ray diffraction, and fluorescence analyses. The main constituent of the salt was determined to be $K_3Na(SO_4)_2$ and then synthesized.

One recovery technique of residual sugar from molasses is the Steffen method using calcium oxide. This treatment discharges waste fluid which is generally concentrated in order to avoid pollution of rivers and sea. General analytical data and the infrared spectra of the concentrated Steffen fluid are summarized and shown in Table 1 and Fig. 1.

How to isolate the components of the concentrated Steffen fluid for manufacturing the products is a matter of interest and importance to the beet sugar industry. This interest in the chemical components led us to isolate the inorganic components and determine their chemical constituents. This paper describes a chemical desalting technique of the concentrated Steffen fluid and the chemical components, and the chemical structure and syntheses of the main constituents of the salt isolated.

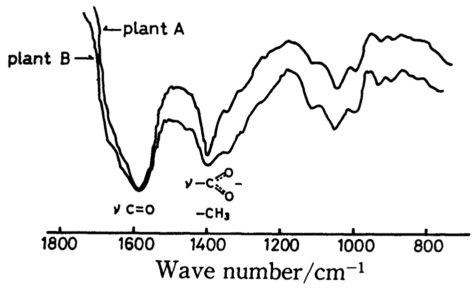

Fig. 1. Infrared spectra of concentrated Steffen fluids applied to KBr disk.

TABLE 1. GENERAL CHEMICAL COMPONENTS OF CONCENTRATED STEFFEN FLUID (pH 9.0)

Solid matter	55%
Carbohydrates, total	13 (sucrose 12.4%)
Reductive carbohydrates	0.2
Nitrogen, total	3.0
Nitrogen, amide	0.7
Nitrogen, betaine	1.1
Sulfate ash	20.0
Sodium	1.5
Potassium	6.6
Calcium	0.01
Phosphorus as P_2O_5	0.01
Others	0.4

It is known that acidification of the concentrated Steffen fluid causes a desalting phenomenon.[1] This elementary knowledge was developed into the desalting process to be reported below. And also, the chemical structure of the main constituent of the isolated salt was determined as tripotassium sodium bis (sulfate) by the X-ray diffraction data and identified by the synthesis starting from the related known inorganic compounds. The by-components and the impurities were identified with the X-ray diffraction data and the fluorescent X-ray data.

Experimental

The IR spectra were determined on a Shimadzu IR-400 spectrometer. The X-ray diffraction and fluorescence analyses were performed on a Toshiba ADG-102 X-ray diffractometer and a AFV-202F X-ray fluorescence spectrometer.

General Procedure for Desalting Treatment of the Concentrated Steffen Fluid. A solution of the concentrated Steffen fluid in methanol, was acidified by addition of a suitable amounts of concd sulfuric acid till pH 4 or 3 of the solution was attained. After standing over night or on chilling, the salt which precipitated was filtered. The salt obtained was recrystallized from water for further purification as needed. Isolation of the salt can be efficiently carried out in *ca.* 20—24% yield for the concentrated Steffen fluid used, and the yield was almost quantitative.

Preparation of Potassium Sodium Sulfate. *Procedure 1*: Aqueous solution of 3 mol of KOH and 1 mol of NaOH was treated with concd sulfuric acid until pH 3 and the salt was deposited by addition of methanol.

Procedure 2: Aqueous solution of 3 mol K_2SO_4 and 1 mol of Na_2SO_4 was concentrated by rotary evaporator until deposition of the salt.

Procedure 3: The salt was deposited from aqueous solution of 3 mol K_2SO_4 and 1 mol Na_2SO_4 by addition of methanol.

Procedure 4: Aqueous solution of 3 mol of K_2SO_4 and 1 mol of Na_2SO_4 was controlled at pH 3 and then salt deposition treatment was carried out by addition of methanol. The results of preparations starting from potassium and sodium compounds are summarized in Table 4.

Results and Discussion

Effective desalting out treatment of concentrated Steffen fluid using concd sulfuric acid in methanol was carried out. Addition of concd sulfuric acid is for the

Table 2. Desalting treatments of concentrated Steffen fluid

Plant A		
Concentrated Steffen fluid, g	665	
Reconcentrated Steffen fluid, g	460	
Salt obtained by acidification using concd H_2SO_4 to pH 3 in MeOH solution, g	163	(24.4%[a])
Plant B		
Concentrated Steffen fluid, g	708	
Salt precipitated by addition of MeOH, g	10.6	(1.5%[a])
Residue after evaporation of MeOH and water, g	406	(57.4%[a])
Salt isolated by acidification of the above residue till pH 3	84.4	(20.8%[a])
Plant C		
Concentrated Steffen fluid, g	1000	
Salt isolated by acidification in MeOH solution till pH 3	225	(22.5%[a])

a) Yields were wt% for concentrated Steffen fluid used.

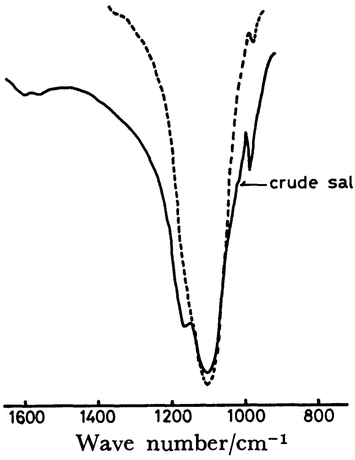

Fig. 2. Infrared spectra of the salts precipitated from Steffen vinasse (KBr-disk).

most efficient precipitation of sulfate salt; the addition of methanol makes a contribution to reduce the solubility of the inorganic salts. Incidentally, methanol alone added to concentrated Steffen fluid or reconcentrated Steffen fluid precipitates the salt in *ca.* 1.5% yield for concentrated Steffen fluid. Furthermore, addition of concd sulfuric acid until pH 4 or 3 of concentrated Steffen fluid or reconcentrated Steffen fluid in methanol solution makes for efficient precipitation of the salt, as shown in Table 2. The salt obtained by the above treatment was crystalline matter, shown in the scanning electron microscopic photographs in Fig. 3.

Infrared spectra of the salts precipitated by addition of methanol alone and by addition of concd sulfuric acid in methanol solution have the characteristic absorption in 1000—1200 cm^{-1} region, as shown in Fig. 2. The IR spectrum of the salts purified by recrystallization from pure water showed an adsorption at 1090 cm^{-1} alone, which suggests it to be a sulfate ion. The shoulder band on the IR spectrum of the crude salt

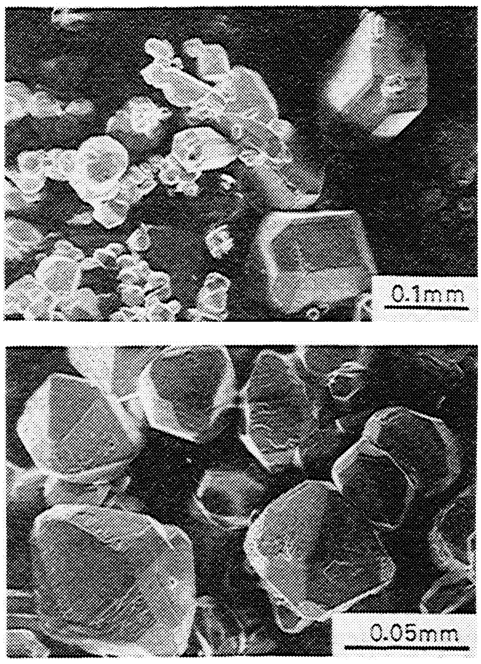

Fig. 3. SEM photographs of the crude salt isolated from CSF.

Table 3. X-Ray diffraction data[a] (time constant; 2 chart full scale; 400/0.6)

$2\theta/°$ (Intensity)	$2\theta/°$ (Intensity)
$K_3Na(SO_4)_2$	
1.422 (65.6)	2.039 (44.4)
1.468 (63.3)	2.189 (41.2)
1.538 (60.1)	2.336 (38.5)
1.601 (57.5)	2.447 (36.7)
1.641 (56.0)	2.642 (33.9)
1.660 (55.3)	2.838 (31.5)
1.717 (53.3)	2.938 (30.4)
1.732 (52.8)	3.675 (24.2)
1.833 (49.7)	4.092 (21.7)
1.852 (49.1)	4.924 (18.0)
$K_2S_4O_6$	$K_2S_3O_{10}$
2.938 (30.4)	3.140 (28.4)
3.056 (29.2)	3.361 (26.5)
3.173 (28.1)	3.847 (23.1)
3.361 (26.5)	4.267 (22.8)

a) Form: Powder, X-ray target: Cu, X-ray-intensity 35-Kvp. 15 ma. Scan speed: 1°/min, Scan range: 70 from 5, Chart speed: 10 mm/min.

Table 4. Syntheses of tripotassium sodium bis(sulfate)

Raw materials	Preparation	Sulfate salt obtained
3KOH+NaOH	Procedure 1	$K_3Na(SO_4)_2$ (*ca.* 60%) and Na_2SO_4 (*ca.* 40%)
$3K_2SO_4+Na_2SO_4$	Procedure 2	$K_3Na(SO_4)_2$ (*ca.* 50%) and K_2SO_4 (*ca.* 50%)
$3K_2SO_4+Na_2SO_4$	Procedure 3	$K_3Na(SO_4)_2$ (100%)
$3K_2SO_4+Na_2SO_4$	Procedure 4	$K_3Na(SO_4)_2$ (*ca.* 80%) and K_2SO_4 (20%)

which appears at slightly higher wavelength (1170 cm^{-1}) should be attributed to the HSO_4^- ion which disappears from the spectrum of the purified salt. The X-ray diffraction data of the crude salt allowed us to the chemical structure of the salt to be $K_3Na(SO_4)_2$ as shown in Table 3; the presence of the compounds $K_2S_4O_6$ and $K_2S_3O_{10}$ were found as by-products in *ca.* 30—40%. The results were confirmed with ASTM data, No. 20928 ($K_3Na(SO_4)_2$), No. 5631 (Na_2SO_4), and No. 5613 (K_2SO_4). The fluorescent X-ray data showed the presence of Cu, Rb, and Zn (below 0.0%) as the small impurities.

The syntheses of tripotassium sodium bis(sulfate) known hitherto as a natural occurring material was carried out starting from the corresponding sulfates or hydroxides and sulfuric acid for the purpose of identification of the salt. It is known[2,3] that potassium sodium sulfate naturally occurs in volcanic districts, *e.g.* the glaserita or aphthitalite $K_3Na(SO_4)_2$ found as an incrustation on Vesuvian lava, in the salt deposit of Douglashall (Westeregeln), at Rucalmuta (Sicily), and in a sea water system, for example B. Gossner[4] regards glaserite as a definite mineral species, but J. H. Van't Hoff and H. Barshall[5] considered it to be a mixture of the two component sulfates: $3K_2SO_4+Na_2SO_4$. An impure form of this salt containing 75 to 85 per cent of K_2SO_4 and 9 to 21 per cent of Na_2SO_4 and known as platosulfate[6] has been separated from a concentration of kelp-liquors.

The authors wish to express their thanks to Hokkaido-Togyo Co., Ltd. for financial support and Dr. Yoshihisa Yamamoto of the Faculty of Pharmaceutical Sciences, Higashi-Nippon-Gakuen University, for his helpful discussion.

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