CHICLE DEVELOPMENT CO., INC.

500 FIFTH AVENUE

NEW YORK

PLEASE ADDRESS ALL COMMUNICATIONS TO THE COMPANY

January 27th 1936

Messrs. P.L. Becker
W.C. Arkell
J.S. Ellithorp
C.F. Dunn
S.C. Prescott
G.R. Cowgill
F. Thamann

Gentlemen:-

Mr. H.W. Conner of the Wm. Wrigley Jr. Company has written me a letter dated January 21st to which he attached copies of Hubbard's Modification of the Method of Wilkins, Willoughby, Kraemer and Smith in connection with Dithizone Methods.

Mr. Conner collected the above information while at Dr. Hubbard's laboratory in Cincinnati and while permission has been granted to distribute this information among the interested parties, by Dr. Hubbard, he wishes this matter to be regarded as confidential by all who use it, as he may later wish to publish it.

Very truly yours,

CHICLE DEVELOPMENT COMPANY

S.S. [illegible],
President

SSY-W

Encl. Copy of Hubbard's Modification of the Method of Wilkins, Willoughby, Kraemer and Smith (Dithizone Method)

cc: NLB

CHICLE DEVELOPMENT CO. INC.

Jan. 21, 1936

Mr. S. S. Yates, Pres.,
Chicle Development Co.,
500 Fifth Ave.,
New York, N. Y.

Dear Mr. Yates:

With the active interest now evinced in comparing alternative Dithizone methods, it might be well to distribute copies of the procedure which has been developed by Hubbard at Cincinnati.

Dr. Hubbard looked over the notes which I took when visiting his laboratory and has given us permission to distribute them among the interested parties. He wishes, however, that the matter be regarded as confidential by all who use it, inasmuch as he may later wish to publish it.

Yours truly,

WM. WRIGLEY JR. COMPANY

per H. W. Conner

HWC:m
-Enc.-

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HUBBARD'S MODIFICATION OF THE METHOD OF
WILKINS, WILLOUGHBY, KRAEMER AND SMITH
(Ind. Eng. Chem., Anal. Ed. 7:33-36-1935.)

Cut 5 g. sample to less than 1 cm. size.

Burn in 100-500 ml. capacity silica evaporating dish over a matted gas flame. After charring is well under way, the surface may be flashed with the flame.

Place in muffle at 500°C. for 1 hour.

Cool, and add 5 ml. conc. HNO_3 (washing down sides).

Heat over open flame to evaporate acid.

Return to muffle for 1/2 hour.

Cool, and add 5 ml. water,
5 ml. NaCl-HCl solution,
2 ml. Concentrated HCl.

Warm to dissolve all ash (except for slight silica residue).

Add 15 ml. ammonium citrate solution. (Will keep iron and calcium in solution.)

Transfer to 150 ml. Squibb separatory funnel.

Add one drop phenol red. Shake.

Make slightly alkaline by adding conc. NH_4OH until indicator changes from red, to yellow, to red. (pH 7.5)

Add 2 ml. KCN solution, (to complex other metals).

Add 5 ml. aliquots of Dithizone #1, separating "X", as Willoughby does, and transfer to a separatory funnel. After extraction of "X" according to Willoughby, 20 ml. of $X(NO_3)_2$ solution is obtained, containing 1% HNO_3.

Add a drop of phenol red and neutralize as before, with NH_4OH.

Add 2 ml. of KCN.

Add 1 ml. aliquots of Dithizone #2 until Dithizone layer is a definite purple, not a pure red.

The Dithizone layer is diluted to 20 ml. with chloroform.

Free Dithizone is removed from the chloroform solution by four 20 ml. aliquots of Winters solution "F".

The red complex is run into 10 ml. of HCl., (concentrated acid diluted with 9 volumes of water) in a clean separatory funnel.

The blue-green Dithizone layer, to which is added 0.15 ml. of absolute ethyl alcohol (with stirring), is then placed in one cup of a colorimeter set at 31 mm. Into the other cup is placed a standard solution of Dithizone in chloroform equivalent to .03 mg. of "X". (The setting of 31 is chosen in preference to setting of 30 since the blank contributes .001 mg. of "X", as an average.)

A determination consists of parallel technique on one or more samples, one blank and one standard based on an initial .03 mg. sample of "X" as $X(NO_3)_2$.

REAGENTS:-

Potassium Cyanide	10 g. in 100 ml. water.
NaCl + HCl	5 ml. conc. HCl diluted to 100 ml. with water and saturated with NaCl at room temperature.
Ammonium Citrate	40 g. citric acid mono-hydrate neutralized with NH_4OH diluted to a liter. (Add 2 ml. of chloroform as a preservative.)
Phenol Red	.04% solution made up with NaOH according to Clark & Lubs.
Dithizone #1	.04 g. Dithizone per liter $CHCl_3$.
Dithizone #2	.1 g. Dithizone dissolved in 30 ml. $CHCl_3$ and extracted in a large separatory funnel with 900 ml. of 1/2% (by volume) NH_4OH. Aqueous phase is separated and neutralized with 10% (by volume) HCl. Precipitated Dithizone is taken up in chloroform and diluted so as to be equivalent to approximately .01 mg. "X" per liter. This solution is stored under $HgSO_3$ (6%).
Winters Solution "F" ...	10 ml. NH_4OH plus 10 ml. of 10% KCN diluted to a liter. Add 5 ml. Dithizone #2 plus 10 ml. $CHCl_3$ in a large separatory funnel. This will leave a de-leaded aqueous solution which retains some yellow ammonium Dithizone complex. Prepare ahead and allow to stand in sunlight to bleach the color.
Standard Lead Solution ..	0.1598 g. $X(NO_3)_2$ plus 10 ml. conc. HNO_3 diluted to 1 liter. Dilute with distilled water 1:10 so that 1 ml. is equivalent to 0.01 mg. of lead.

(Dithizone from Eastman.
HCl, HNO_3, NH_4OH are Grasselli C.P. Grade.
Remaining reagents are Merck blue label reagent grade.)