This document was produced by scanning the original publication.

Ce document est le produit d'une numérisation par balayage de la publication originale.

DECLASSIFI	ED
DATE 1963	
AUTHORIZED BY	hn

CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 61-113

THE DETERMINATION OF CHLORIDE CONTENT IN THREE ZINC OXIDE SAMPLES FROM HUDSON BAY MINING AND SMELTING CO. LIMITED, FLIN FLON, MAN.

by

L. G. RIPLEY & W. R. INMAN

MINERAL SCIENCES DIVISION

NOTE: THIS REPORT RELATES ESSENTIALLY TO THE SAMPLES AS RECEIVED. THE REPORT AND ANY CORRESPONDENCE CONNECTED THEREWITH SHALL NOT BE USED IN FULL OR IN PART AS PUBLICITY OR ADVERTISING MATTER.

COPY NO. 17

SEPTEMBER 8, 1961



Mines Branch Investigation Report IR 61-113

THE DETERMINATION OF CHLORIDE CONTENT IN THREE ZINC OXIDE SAMPLES FROM HUDSON BAY MINING AND SMELTING CO. LIMITED, FLIN FLON, MAN.

> by L.G. Ripley^{*} and W.R. Inman^{**}

SUMMARY OF RESULTS

The total chloride concentration in the submitted zinc oxide samples has not been determined because no suitable method was found applicable for the <u>insoluble</u> chlorides. The <u>soluble</u> chlorides in the range of 0.01 to 0.03% have been determined within the accuracy of $\stackrel{+}{-}$ 0.004% by the isolation of the <u>soluble</u> chlorides by a steam distillation procedure followed by a potentiometric titration. An alternative colorimetric method, with the same accuracy, is described.

Leaching and fusion solution techniques have been found to be unreliable in the range of chloride concentrations of 0.01 to 0.03%.

** Senior Scientific Officer and Head, Analytical Chemistry Subdivision, Mineral Sciences Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

CONTENTS

	Page
Summary of Results	. 1
Introduction	, 1
Experimental Details	. 2
A. Potentiometric Titration Procedure with	
Silver Nitrate	, Z.
1. Apparatus	, 2
2. Reagents	, Z
4. Titration Procedure	, Э Б
	, ,
B. Colorimetric Procedure with $Hg(SCN)_2$ -Fe(ClO ₄) ₃ .	, 6
1. Apparatus	, 6
2. Reagents	, 6
3. Sample Preparation	, 7
4. Colorimetric Procedure	, 9
Results and Discussion	, 10
1. Undesirable Side Reactions	. 10
2. Insoluble Chlorides	, 15
Conclusions	, 20
Acknowledgments	, 20
References	. 21
Appendix	. 22 - 26

- --

INTRODUCTION

Three samples of zinc oxide were submitted by Hudson Bay Mining and Smelting Company Limited, Flin Flon, Manitoba, in connection with a request for a suitable procedure for the determination of chloride, which would have enough sensitivity to allow the accurate determination of total chloride to 0.001%. (Correspondence relative to this investigation is included in the Appendix).

These zinc oxide samples were received by the Analytical Chemistry Subdivision on July 13, 1960, and were identified by the following laboratory numbers:-

> Lab. No. 3979/60 - Zinc Oxide Fume Lab. No. 3980/60 - Smelter Stack Dust Lab. No. 3981/60 - Moore Residue

The range of chloride ion reported for these samples was from 0.01 to 0.02%.

The determination of chloride in the range 0.01 to 0.02% with an accuracy of 0.001% is not easy. Two approaches have been tried:-

a) Potentiometric titration with silver nitrate (1).

b) Photometrically by the mercuric thiocyanateferric perchlore method (2).

Both of these methods have proved reasonably satisfactory.

EXPERIMENTAL DETAILS

A. Potentiometric Titration Procedure with Silver Nitrate

1. Apparatus

A Leeds and Northrup, ac operated No. 7664 pH indicator was used with a pure silver electrode No. 1261 (Beckman, Billet style) and a silver-silver chloride reference electrode No. 1199-72 (Leeds and Northrup).

2. Reagents

a) 0.05 N silver nitrate: 8.5 g of Merck reagent grade silver nitrate was dissolved in distilled water and diluted to 1 litre, (1 ml is equivalent to 0.00180 g chloride ion).

b) Potassium chloride solution: 1 g of Baker analyzed reagent potassium chloride, certified assay, KCl = 99.7%, (dried at 110°C for 1 hour) was dissolved in distilled water and diluted to 1 litre, (1 ml is equivalent to 0.0004756 g of chloride ion).

The silver nitrate solution was standardized against an aliquot of a blank solution which had a 10 ml aliquot of the above potassium chloride solution added, and the resulting solution titrated under similar acid and temperature conditions as described for the samples.

- 2 -

3. Sample Preparation

The samples, which were used directly as received, were dissolved by the following methods:-

a) Leaching (1% sodium hydroxide) method of solution

In this method a sample weight of 10 g was heated with 100 ml of 1% sodium hydroxide solution for 1 hour. After cooling, the solution was filtered through a Whatman No. 41 H paper. The filtrate was reserved for potentiometric titration.

b) Steam distillation procedure

Figure 1 shows the assembled apparatus.

A sample weight of 10 g was placed in the reaction flask. When the apparatus was assembled and the receiver which contained 100 ml of 2% sodium hydroxide solution was in place, 10 ml of water and 35 ml concentrated sulphuric acid were added through the funnel.

The heater was turned on to heat the reaction flask to 135°C, then the steam was admitted to the reaction flask and the hydrogen chloride, which was produced, was distilled at a reaction flask temperature of 150°C until 400-500 ml of distillate was obtained.

The distillate was cooled, neutralized and made 5% acidic with respect to sulphuric acid, and 5 ml concentrated nitric acid was added. A 10 ml aliquot of a potassium chloride solution (10 ml is equivalent to 0.004756 g chloride ion) was added. The solution was then cooled to less than 10°C and titrated with silver nitrate potentiometrically.

- 3 --



ų

Figure 1 - Steam Distillation Apparatus

T - Steam Distination Apparatus

A reagent blank solution was prepared by the above procedure and was treated under the same conditions as the samples.

4. Titration Procedure

The progress of the titration with 0.05 N silver nitrate was followed by plotting on No. 315 F graph paper the potential produced after each addition of the reagent. The additions were varied from 1.0 to 0.10 ml, the smallest being used in the region of the end-point. The actual end-point was then determined by calculating the point of inflection which is obtained by projection lines as in Figure 2. The mid point, C, of the line AB is the point of inflection and also the end-point.

Figure 2 - Typical Chloride Titration Curve

- 5 -

The difference in titre required for the blank solution, which contained a 10 ml potassium chloride addition, and the titre of the sample solution, which also contained a 10 ml potassium chloride addition, was the true titration of the sample solution.

B. <u>Colorimetric Procedure with $Hg(SCN)_2 - Fe(ClO_4)_3</u></u>$

1. Apparatus

A Beckman B spectrophotometer, with 1 cm and 5 cm cuvettes, was used.

2. Reagents

a) Mercuric Thiocyanate: a saturated aqueous solution (=0.07%), was prepared by dissolving 1.000 g mercuric thiocyanate, Fisher certified reagent, in 1 litre of distilled water. This solution was heated to near boiling for 1 hour, then cooled overnight to room temperature, and filtered to remove the excess mercuric thiocyanate.

b) Ferric Perchlorate Solution: 14 g of pure iron (NBS No. 55D) was dissolved in 1:1 nitric acid, then 120 ml of perchloric acid (70%) was added and the solution taken to fumes. After cooling, the solution was diluted to 1 litre with distilled water.

c) Perchloric Acid; Nichols Chemical Co. (70-72%) reagent grade.

d) Potassium Chloride Stock Solution: 1 g of dried potassium chloride was dissolved in distilled water and diluted to
1 litre. A 20 ml aliquot of this solution was diluted to 500 ml
(1 ml is equivalent to 0.000019 g chloride ion).

3. Sample Preparation

The three zinc oxide samples were dissolved by the following methods:-

a) Leaching (1% sodium hydroxide) method of solution

This method required a l g sample which was heated with 100 ml of 1% sodium hydroxide solution for l hour. After cooling, this solution was filtered through a Whatman No. 41 H paper. The filtrate was made up to 200 ml and 50 ml aliquots were taken for the colorimetric procedure.

b) Sodium carbonate fusion

One g samples were mixed with 5 g sodium carbonate in a nickel crucible (with a cover) and fused for 30 minutes over an air-gas flame. The melt was dissolved with water and filtered through a Whatman No. 41 H paper into a 200 ml volumetric flask and made up to volume; 50 ml aliquots were used for the colorimetric procedure.

c) <u>Sodium carbonate with either sodium nitrate or</u> potassium nitrate fusion

One g samples were mixed with 5 g of sodium carbonate and 1 g of either potassium nitrate or sodium nitrate and fused for 30 minutes. The melt was leached with water, filtered, and made up to volume as in b).

d) Steam distillation procedure

This method requires the apparatus as shown in Figure 1.

A sample weight of 10 g was placed in the reaction flask. When the apparatus was assembled and the receiver which contained 100 ml of 3% sodium hydroxide solution^{*} was in place, 10 ml of water, 35 ml concentrated sulphuric acid and 5 ml concentrated nitric acid were added through the funnel.

The distillation procedure, which was the same as described earlier, was carried on until approximately 500 ml of distillate was obtained.

The receiver was removed and heated on a hot plate to reduce the volume to 450 ml. It was then cooled and made up to 500 ml in a volumetric flask. Aliquots of 25 ml were used for the colorimetric procedure.

The strength of this reagent is increased, from the quantity specified on page 3, to neutralize the distilled nitric acid which was not present previously.)

4. Colorimetric Procedure

Chlorides can be determined spectrophotometrically using a method based on the following equations:-

$$3 \text{Hg}(\text{SCN})_2 + 6 \text{C1}^- \longrightarrow 3 \text{HgCl}_2 + 6 \text{SCN}^-$$

 $6 (\text{SCN})^- + 2 \text{Fe}^{+++} \longrightarrow \text{Fe}_2 (\text{SCN})_6$

The red coloured ferric thiocyanate complex, which is indicative of the chloride content, has a minimum absorbancy at $460m\mu$.

The procedure followed was to place a suitable aliquot of a sample solution, obtained from one of the described solution methods, in a 100 ml volumetric flask. The reagents were added in the following order, 10 ml of perchloric acid, 10 ml of aqueous mercuric thiocyanate, and 10 ml of ferric perchlorate. The solution was diluted to volume with distilled water.

A blank was carried through the same solution technique, aliquotting, and reagent additions as the sample solutions. The colour intensity was read, after 10 minutes, in 5 cm cuvettes at $\lambda = 460$ mµ.

A standard curve was prepared using aliquots of the blank solution to which aliquots of the standard potassium chloride solution (1 ml is equivalent to 0.000019 g chloride ion) were added. The coloured complex was developed as described above.

RESULTS AND DISCUSSION

1. Undesirable Side Reactions

The steam distillation of the zinc oxide samples produced some undesirable side reactions when nitric acid was not used:

 (a) In sample No. 3980, a yellow solid co-distilled.
 This material was identified as S plus Se by X-ray fluorescence analysis.

(b) In sample No. 3981, a colourless gas co-distilled which turned the alkaline solution in the receiver a yellowish colour. This material is believed to be organic, but its identification was not possible because its X-ray diffraction pattern was not recorded in the A.S.T.M. card index. Also, the infra-red spectrum pattern was not available in the literature.

There was no evidence that the co-distilled by-products caused any interference in the potentiometric titration procedure. But these co-distillates definitely interfered in the colorimetric procedure. In the case of sample No. 3980, the colour intensity was greatly increased, which would give an erroneous chloride result. When an aliquot of this distillate was mixed with the mercuric thiocyanate aliquot and allowed to stand, turbidity was soon noticed and after several hours a black precipitate was obtained, which

- 10 -

X-ray fluorescence indicated to be a mercury compound. The explanation appears to be that the interferants (likely sulphur plus selenium) attacked the mercuric thiocyanate releasing free thiocyanate ion, which combined with the ferric iron to give the increased colour, and at the same time some insoluble mercury compound was produced. In the case of sample No. 3981, a chloride content of 0.031% was indicated, whereas, other tests have shown the chloride ion to be absent. Whether this absorbancy was directly due to coloured distillate, or if there was an attack on the mercuric thiocyanate as in sample No. 3980, was not determined.

When 5 ml concentrated nitric acid was added to the reaction flask along with the sulphuric acid before distillation, these two side reactions were practically eliminated. However, the presence of nitric acid is not desirable as it could oxidize the chloride ion to chlorine, some of which might escape from the receiver. Actually, no chlorine was lost during distillation of synthetic solutions containing a 10 g sample plus a known potassium chloride addition when 5 ml nitric acid was used. But when 25 g samples were treated with 50 ml sulphuric acid plus 10 ml nitric acid plus 5 ml water and distilled, some chlorine losses were noticed as shown in Table 1.

TABLE 1

Method	Per cent Cl						
	No. 3979	No. 3980	No. 3981				
10 g, H ₂ SO ₄ only (KCl added) titrated at <10°C	0.028(1)*	0.028 (1)	Nil (1) '				
10 g, H ₂ SO ₄ + HNO ₃ (KCl added) titrated at room temperature	0.027 - 0.001 (3)	0.0026 ⁺ 0.004 (3)	Nil (3)				
25 g, H ₂ SO ₄ + HNO ₃ (KCl added) titrated at room temperature	0.017 - 0.003 (2)	0.006 + 0.000 (2)	Nil (1)				
25 g, H ₂ SO ₄ only (KCl added) titrated at room temperature	 ,	0.026 ⁺ 0.001 (2)					

Effect of Nitric Acid on Hydrogen Chloride Distillations

*Bracketed figure indicates the number of determinations.

There appears to be no appreciable chlorine loss when 5 ml nitric acid was used with 10 g samples.

The presence of nitric acid in the receiver would cause no interference in a potentiometric titration. However, it causes a slight lowering of the colour intensity in the colorimetric procedure as shown in Table 2.

TABLE 2

Sample	C1	ml HNO ₃ present	% Transmittance
Blank		1 44 148	100
1	95γ	0.1	58.8
2	95γ	0.3	60.0
3	95γ	0,5	60.5

Effect of Nitric Acid in the Colorimetric Procedure

In actual practice, the 5 ml of nitric acid, which was added in a distillation, would represent a maximum of 0.25 ml in the aliquot taken for colour development; therefore, a slightly lower colour intensity would be expected when nitric acid was used.

A comparison of the chloride percentages obtained by potentiometric and colorimetric procedures following a steam distillation, with and without nitric acid being added, is shown in Table 3.

TABLE 3	
---------	--

Comparison of Colorimetric and Potentiometric Results

Preparation	Analysis	Per cent Cl				
Method	Method	No. 3979	No. 3980	No. 3981		
l0 g sample H ₂ SO ₄ only	* Colorimetric Potentiometric	0.038 0.028	too much colour 0.028	0.031 Nil		
25 g sample H ₂ SO ₄ only	Potentiometric		0.026 - 0.001 (2)			
10 g sample $H_2SO_4 + HNO_3$	Colorimetric Potentiometric	$\begin{array}{c} 0.024 \stackrel{+}{-} 0.003 (3) \\ 0.027 \stackrel{+}{-} 0.001 (3) \end{array}$	$\begin{array}{c} 0.024 \stackrel{+}{-} 0.001 (3) \\ 0.026 \stackrel{+}{-} 0.004 (3) \end{array}$	$\begin{array}{c} 0.001 \stackrel{+}{-} 0.0009 (3) \\ 0.000 \stackrel{+}{-} 0.000 (3) \end{array}$		

* Interferences were present - 14 -

It is observed from Table 3, that nitric acid was essential in the colorimetric procedure, which then gave concordant results with the potentiometric approach.

2. Insoluble Chlorides

A defect in the steam distillation procedure lies in the fact that the samples are not completely dissolved; hence some insoluble chlorides, e.g., silver chloride, might be present and not accounted for in the chloride determinations.

A semi-quantitative spectrographic analysis indicated the following impurities:

TABLE 4

				Per	cent				
Sample	Ba	As	Si	B	Mn	Al	Fe	Sb	Mg
No. 3979	0.01	0.8	0.7	Tr.	0.0006	0.6	0.5	0.1	0.009
No. 3980	0.04	2	2	0.003	0.01	2.5	4	0.1	0,2
No. 3981	n.d.	0.9	2	n.d.	0.04	1.5	P.C.	n,d.	0.3
	\mathbf{Pb}	Sn	Cr	v	Ca	Cd	Cu	Zr	Ag
No. 3979	1	0.004	Tr.	0.002	0.1	0.06	0.1	0.002	0.001
No. 3980	6 .	0.02	Tr.	0.004	0.6	3	6	0.005	0.01
No. 3981	0.5	Tr.?	Tr.	0.003	1 ·	0.09	1	Tr.	0.01
	Zn	Ti	Ni	Co	Bi	P	Ge	Be	
No. 3979	P.C.	0.05	Tr.	Tr.	Tr.	Tr.	Tr.?	n.d.	
No. 3980	P.C.	0.1	0.002	Tr.	0.05	n.d.	Tr. ?	Tr.	,
No. 3981	P.C.	0.04	0.002	0.04	n.d.	n.d.	n.d.	n.d.	
	L		<u> </u>	J	/	1	L <u></u>	I	J

Semi-quantitative Spectrographic Analysis

If all the silver is present as silver chloride, then the maximum insoluble (and undetermined) chloride would be 0.0032%.

Insoluble silver chloride can be readily dissolved with a sodium carbonate fusion (1). When this was tried, some of the melt condensed on the lid of the crucible suggesting the possibility that some volatile chlorides, e.g., arsenous chloride, might have escaped. To avoid this condition, sodium nitrate or potassium nitrate was added to the fusion mixture to ensure that all the arsenic was in the pentavalent state and thereby achieve a negligible chloride loss. Since only 1 g samples can be adequately fused at one time, only the colorimetric procedure would be applicable for the determination of chlorides.

No evidence was found that the presence of the sodium carbonate, sodium nitrate, potassium nitrate or zinc oxide caused any real interference in their own right. However, since the colorimetric curve for chloride does not obey Beer's Law, there is an inherent background effect present (2). This effect is caused because the standard curve is dependent on the background chloride as well as the difference in chloride level between the blank and the sample. Figure 3 shows this effect when four background media are used.

Figure 3 - Effect of Background Chloride from Fusion Mixtures

- 17 -

The four background media shown in Figure 3 are as follows:-

a) Distilled water.

b) Aliquots of a solution resulting from a sodium carbonate fusion - each aliquot contained 1.0 g of sodium carbonate.

c) Aliquots of a solution resulting from a sodium carbonate plus sodium nitrate fusion - each aliquot contained 1.0 g sodium carbonate and 0.2 g sodium nitrate.

d) Aliquots of a solution resulting from a sodium carbonate plus potassium nitrate fusion - each aliquot contained 1.0 g sodium carbonate and 0.2 g potassium nitrate.

In each case, a standard curve was prepared by using aliquots of the above solutions, to which aliquots of stock potassium chloride solution were added.

The error due to this effect becomes minimal when the standard curve is prepared under the same conditions as the sample.

However, the background effect was lower in the steam distillation method because larger sample weights were used. This means that the quantity of background chloride present in the aliquot required for colorimetric development was less than it was in the aliquots required from the leaching or fusion decomposition procedures.

The comparison of determinations obtained from the various decomposition procedures is shown in Table 5.

TABLE 5

Comparison of Determinations Following Various Decomposition Procedures

Method of Sample	Per cent Cl					
Preparation	No. 3979	No. 3980	No. 3981			
1% NaOH leaching - titration	0.027 - 0.005 (3) +	0.017 - 0.003 (3)	Nil (3)			
Distillation without HNO ₃ - titration	0.028 (1)	0.028 (1)	Nil (1)			
Distillation with HNO ₃ - titration	0.027 + 0.001 (3)	0.026 - 0.004 (3)	Nil (3)			
1% NaOH leaching - colorimetric	0.031 ⁺ 0.001 (2)	0.033 - 0.005 (2)	0.011 - 0.002 (2)			
Na ₂ CO ₃ fusion - colorimetric	0.052 + 0.017 (6)	0.041 + 0.012 (6)	0.021 + 0.006 (6)			
Na ₂ CO ₃ + NaNO ₃ fusion - colorimetric	0.019 (1)	0.026 (1)	Nil (1)			
Na ₂ CO ₃ + KNO ₃ fusion - colorimetric	0.045 (1)	0.033 (1)	0.042 (1)			
Distillation with HNO ₃ - colorimetric	0.024 - 0.003 (3)	0.024 - 0.001 (3)	0.001 - 0.0009 (3)			

*Bracketed figure indicates the number of determinations.

CONCLUSIONS

This investigation shows that the best procedure to be followed in order to achieve a reliable chloride determination, in the range requested and in the type of samples submitted, would be an isolation of the soluble chlorides by steam distillation followed by a potentiometric titration. A good alternative method would be the colorimetric analysis, subsequent to the soluble chloride isolation by steam distillation.

The leaching and fusion techniques, followed by a colorimetric determination of the chlorides, are not too reliable, due to background effect caused by the chlorides present in the reagents, which results in uncertain standard curves and in erratic chloride values for the unknown samples.

ACKNOWLEDGMENTS

The authors thank the following personnel: Miss F. Goodspeed for infra-red spectrum analysis, Mrs. D. Reed for X-ray fluorescent analysis, Miss E. Kranck for semi-quantitative spectrographic analysis, J.F. Rowland and E.J. Murray for X-ray diffraction analysis, and R. Donahoe who assisted with the potentiometric titrations and with the colorimetric determinations.

REFERENCES

- L.G. Ripley and W.R. Inman, "The Potentiometric Titration of Chlorides", Mines Branch Investigation Report IR 61-111, (1961).
- (2) L.G. Ripley and W.R. Inman, "Photometric Determination of Chlorides", Mines Branch Investigation Report IR 61-112, (1961).

.....

LGP:WRI/DV

- 22 -

HUDSON BAY MINING AND SMELTING CO., LIMITED FLIN FLON, MANITOBA

May 27, 1960.

Mr. W.R. Inman, Chief Chemist, Mineral Sciences Division, 555 Booth Street, OTTAWA 1, Ontario.

Dear Bob:

Recently we have encountered an analytical problem in our laboratories on which I thought you might be able to help us.

We wish to conduct a chloride survey on some of our plant materials, and in order to do so require an analytical method with enough sensitivity to allow the accurate determination of total chlorides to 0.001%. Two typical examples of these materials are a fumed zinc oxide assaying 71% Zn, 2.4% Pb, 1% Fe, 1% As, .01% Cl and a smelter stack dust assaying 36% Zn, 18% Pb, 4% As, 2% Fe, 1% Cu, 1% Cd and .04% Cl.

Our present method consists of first distilling the chlorides from a 25 gram sample to which sulfuric acid has been added, and then determination of the distilled chlorides by the conventional silver chloride gravimetric procedure. Due to the low chloride content of the materials and limitations in the sample size that can be handled, we are unable to achieve accuracy beyond the second decimal place. This is not sufficient accuracy to give the desired evaluation to the survey of our plant materials.

If you have any suggestions or analytical methods which might be applicable to this problem they would be greatly appreciated.

Best regards,

Yours very truly,

J.N. Kirkbride, Senior Research Engineer. Mineral Sciences Division, A.T. Prince, Chief.

> 555 Booth Street, Ottawa 1, Ontario. June 3, 1960.

Mr. J.N. Kirkbride, Senior Research Engineer, Hudson Bay Mining and Smelting Co., Limited, Flin Flon, Manitoba.

Dear Jack:

Your letter of May 27 regarding the determination of small amounts of chloride has been discussed with some of the staff who have met somewhat similar problems recently.

As a first guess we would suggest that you go along with the distillation but try a volumetric finish. If you collect the HCl in a standard alkali you could back titrate with N/500 acid. This should give the required sensitivity. We have also used a AgNO₃ titration with electrometric end-point. I am having this written up and sent to you in a few days.

If you would like to send us a couple of pounds of the material we could see what results we can get. You might give us the analyses so we will be able to go directly to the Cl determination.

Yours very truly,

W.R. Inman

HUDSON BAY MINING AND SMELTING CO., LIMITED FLIN FLON, MANITOBA

June 6, 1960.

Mr. W.R. Inman, Chief Chemist, Mineral Sciences Division, 555 Booth Street, OTTAWA 1, Ontario.

Dear Bob:

Thank you for your letter of June 3rd and the information regarding the determination of small amounts of chloride.

We shall look forward to receiving the AgNO₃ titration method using an electrometric end-point and in the meantime will try your suggestion of a volumetric finish after distillation.

Your offer to run chloride determinations on some of our material is much appreciated. I will have some samples, along with their analyses, sent to you later in the week.

Thank you again for your cooperation on this problem.,

Yours very truly,

J.N. Kirkbride

HUDSON BAY MINING AND SMELTING CO., LIMITED FLIN FLON, MANITOBA

July 5, 1960.

Mr. W.R. Inman, Chief Chemist, Mineral Sciences Division, 555 Booth Street, OTTAWA 1, Ontario.

Dear Bob:

I am taking advantage of your kind offer to run total chlorides on some of our plant materials, and three samples of these are being forwarded to you.

The analysis of the major elements with the exception of iron is as follows.

Sample	· <u>Zn%</u>	<u>Cu%</u>	$\underline{Cd\%}$	As%	$\underline{Sb\%}$	Pb%	<u>C1%</u>
Zinc Oxide Fume	73.2	0.13	0.04	0.98	0.14	2.3	0.02
Smelter Stack Dust	34.7	1.95	1.43	4.59	0.27	13.3	0.02
Moore Residue	22.6	0.91	0.10	0.68	0.18	0.4	0.01

We shall certainly appreciate anything you may be able to do towards a more accurate chloride determination on these samples.

Best regards.

Yours very truly,

J.N. Kirkbride, Senior Research Engineer.

HUDSON BAY MINING AND SMELTING CO., LIMITED FLIN FLON, MANITOBA

July 6th, 1960.

W.R. Inman, Esq., Chief Chemist, Mineral Sciences Division, 555 Booth Street, OTTAWA 1, Ontario.

Dear Sir:

Re: Our File General 7-M I.O. Reqn. No. 80179

At the request of our Research Department we are forwarding to you via Express, as per copy of receipt attached, one parcel Ore Samples.

Trusting shipment reaches you in good order.

Yours very truly,

J. Putney, Storekeeper.