# Coulometric Determination of Hydrogen Cyanide in Cigarette Smoke\*

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## INTRODUCTION

Several methods (1-5) have been developed for the determination of hydrogen cyanide (HCN) in cigarette smoke. These methods, which include the use of colorimetry, ion-selective electrodes, titration, and gas chromatography, can be classified as non-coulometric. All have certain disadvantages.

Colorimetric determinations of HCN are usually based on a König synthesis, wherein the reaction of cyanogen bromide or chloride with pyridine and an aromatic amine to form a dye involves the use of multi-stage processes and several reagents. Ion-selective cyanide electrodes, described by Viceroy and Grant (3), proved to be unreliable in our laboratory, especially for analyzing wholesmoke solutions that adsorb onto the electrode and cause erratic results.

Mattina (1) described a potentiometric titration for cyanide and sulfide in cigarette smoke. He collected the two components on Ascarite absorbent and performed a potentiometric titration with a standard silver nitrate solution. The plotted data gave two equivalence points, representing sulfide and cyanide. Evaluations of this method have shown that the Ascarite material contains a titratable impurity that gives an end point at the same potential as the sulfide. The titration requires several minutes to complete, and additional time is required for plotting the data and locating the end points.

Brunnemann (2) used a gas chromatographic method based on the conversion of HCN to cyanogen chloride with chloramine-T. The cyanogen chloride was extracted into hexane and analyzed by using a gas chromatograph equipped with an electron-capture detector. This method is lengthier and more sophisticated than needed for routine use.

In 1958 Przybylowicz (6) developed a titration method

for the determination of cyanide by use of coulometrically generated mercury (II) ions, which produce more accurate and reproducible results than do silver ions.

The method described in this paper is a modification of Przybylowicz's. A stationary silver wire coated with mercury is used as a generating electrode and a silver wire treated with sodium sulfide serves as an indicating electrode. Przybylowicz used a phosphate buffer solution of pH 9.2 as a titration medium and worked with generating currents up to 50.95 mA. In the present study, a pH 11 (phosphate-sodium hydroxide) buffer solution is needed to prevent loss of cyanide during titration. The typical generating current used for cyanide in cigarette smoke can be 0.3 mA, and very dilute solutions of cyanide, in concentrations of  $1 \times 10^{-6}$  to  $1 \times 10^{-5}$  g CN<sup>--</sup>, can be titrated. The use of dilute smoke solutions greatly extends the life of the generating electrode and minimizes interference from other smoke components. Initially, a Leeds and Northrup constant-current coulometer was used in developing the method. Since then, a constant-current coulometer with a continuously variable output of 0 to 2 mA was constructed for these determinations. A highimpedance potentiometer with a digital display and output terminals for a strip-chart recorder is incorporated into the instrument. These features eliminate the need for an external millivoltmeter. A strip-chart recorder connected to the output terminals allows a potentiometric titration curve to be drawn automatically during the titration.

The end point is located and cyanide microequivalents can be calculated from the microcoulombs generated. The calibrated chart speed provides a convenient way to determine generation time, from which the amount of mercury (II) ions consumed at the end point can be calculated.

The method is rapid and simple; it requires few reagents; it is semi-automatic and provides a direct measure of cyanide in aqueous solutions.

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# **EXPERIMENTAL**

# Solutions and Reagents

Sodium Hydroxide Solutions: A 0.1 M NaOH solution was prepared for use in the smoke scrubber flask, and a 1.0 M NaOH solution was prepared for use with 0.5 M Na<sub>3</sub>HPO<sub>4</sub> as a pH 11 titration medium.

Disodium Hydrogen Phosphate Solution: A 0.5 M Na<sub>2</sub>HPO<sub>4</sub> solution was prepared by dissolving 134 g of Na<sub>2</sub>HPO<sub>4</sub> 7H<sub>2</sub>O in 1 l of H<sub>2</sub>O.

Sodium Sulfide Solution: A  $5^{0/0}$  aqueous solution was prepared by dissolving 5 g of Na<sub>2</sub>S in 95 ml of distilled water. (This solution is used to treat the silver indicator electrode.)

Buffer Solution (pH 11): This solution was prepared by combining 176 ml of 1.0 M NaOH and 824 ml of 0.5 M Na<sub>2</sub>HPO<sub>4</sub> solution.

Aqueous Lead Acetate: A stock solution of 0.1 M  $Pb(CH_sCOO)_2$  was prepared and 1 ml was diluted to 100 ml with distilled water to make a 0.001 M solution. This solution (4 ml) was added to the titration solution to precipitate any soluble sulfide.

Mercury: Distilled mercury was used to coat the No. 14 silver-wire anode used for coulometric generation of mercury (II) ions.

# Equipment and Apparatus

- The instrument consisted of a constant-current coulometer with a continuously variable output current of 0 to 2 mA and a built-in potentiometer. Output terminals were provided for a strip-chart recorder.
- 2. A Hewlett-Packard strip-chart recorder (Model 7101B) was used to record the potentiometric titration curves.
- 3. The indicating electrodes consisted of a double-junction reference electrode (Orion No. 90-02-00) and a No. 14 silver wire.
- 4. The anode (generating electrode) consisted of a No. 14 spiral-wound silver wire (surface area 4.8 cm<sup>2</sup>) coated with mercury. The cathode was a No. 14 platinum wire isolated from the titration media by placement in a buffer solution (pH 11) contained in an 8 cm × 1.1 cm inside diameter (I.D.) tube fitted with a fine-glass frit.
- 5. A special smoke scrubber flask (Figure 1) was used to collect the HCN from the cigarette smoke.
- 6. A single-port Phipps and Bird smoking machine (cat. No. 9900-300) was used for smoking of test cigarettes.

### Treatment and Care of the Electrodes

The sensitivity of the silver-wire indicator electrode was considerably improved by immersing it in a  $5 \, 0/_0$  sodium sulfide solution for about 30 s before use. How often this treatment is needed was not determined, but no decrease in sensitivity was noticed after several titrations. (Caution: Sodium sulfide is toxic and liberates toxic H<sub>2</sub>S gas in contact with acid. Appropriate precautions should be observed.) Because dilute smoke solutions were used, both the indicator and generator electrodes appeared to last indefinitely with proper treatment.

After a titration was completed, the electrodes were rinsed with distilled water. The generator electrode should be cleaned in concentrated ammonium hydroxide after 6 to 8 titrations. The generator electrode should also be coated with mercury about once or twice a week when in constant use.

#### Procedure

Two or more cigarettes were smoked at standard conditions (one 35 ml, 2 s puff per min) to a 23 mm butt or to within 3 mm of the overwrap, if they were filter cigarettes. During puffing, the whole smoke was scrubbed through 50 ml of 0.1 M NaOH to collect the HCN (Figure 1). After smoking was completed, the contents of the scrubber

Figure 1. Schematic diagram of smoke collection unit.



were transferred to a 100 ml volumetric flask. The scrubber was rinsed twice with 20 ml portions of 0.1 M NaOH, which were also added to the flask. The 0.1 M NaOH solution was finally used to dilute the scrubber solution to the mark. A 5 ml aliquot of sample was transferred to the titration cell (Figure 2), which contained 35 ml of the pH 11 buffer solution and 4 ml of 0.001 M lead acetate solution. The generator electrodes were connected to the coulometer, and the indicator electrodes were connected to the terminals of a potentiometer built into the instrument. The output of the potentiometer was connected to a Hewlett-Packard strip-chart recorder (Figure 3). The recorder was turned on and, when the pen was even with a chart line, the coulometer was started. The potentiometric titration was automatically recorded.

#### Figure 2. Schematic diagram of coulometric titration cell.



Figure 3. Block diagram of coulometric titration system.



The end point was located by means of a plastic template with concentric arcs (Figure 4). This device consists of a transparent plastic square (6 in. square) containing concentric arcs of increasing radii originating at a hole  $(^{1}/_{16}$  in. diameter) in one corner of the square. The template was positioned over the potentiometric titration curve, and the best fitting arc was superimposed on each portion of the curve in turn. A point was then made through the hole in the template, and a line was drawn between the two points. The equivalence point was located where the line bisected the titration curve.

Figure 4. Template with concentric arcs for determining end point.



# Extraction and Analysis of Cyanide Trapped on Filters

Cyanide trapped by the filters was extracted with 25 ml of 0.1 M sodium hydroxide. A 5 to 15 ml aliquot of the extract was titrated coulometrically to determine the amount of cyanide. The cyanide delivered through the filter was collected in the basic aqueous scrubber previously described, and an aliquot was titrated.

# Calibration

A known solution of sodium cyanide  $(2 \times 10^{-3} \text{ M})$  was titrated periodically to ensure that the instrument was operating properly.



# **RESULTS AND DISCUSSION**

Mercury (II) ions are generated and react as follows:  $Hg^0 \rightleftharpoons Hg^{+2} + 2e$ ;  $Hg^{+2} + 2 CN^- \rightleftharpoons Hg(CN)_2$ . Theoretically, one electron equivalent is displaced for each CN<sup>-</sup>. That the coulometric titration curve should correspond to a 1:1 reaction was confirmed experimentally by titration of a known cyanide solution. A typical potentiometric titration curve of CN<sup>-</sup> is shown in Figure 5. The micrograms of CN<sup>-</sup> are calculated from the following equation:

$$\mu g CN^{-} = \frac{T \times M \times E \times 1000}{96,487}$$

where

- T = time in seconds ,
- $M = molecular weight of CN^{-}$ ,
- E = milliamperes.

The relative standard deviation and average recovery of the coulometric titration of a known cyanide solution were  $1.64 \,^{0}/_{0}$  and  $100.3 \,^{0}/_{0}$  (Table 1). The results of HCN determinations on smoke from a filter cigarette by coulometric titration and by a spectrophotometric analysis were in good agreement and had about the same relative standard deviation,  $5.31 \,^{0}/_{0}$  by coulometric titration and  $6.42 \,^{0}/_{0}$  by spectrophotometric analysis (Table 2). [The spectrophotometric method was adapted to the analysis of cigarette smoke from a method published by *Aldridge* (7).]

Several cigarettes, including Kentucky 1R1 standard cigarettes, non-vented-filter cigarettes, non-filter cigarettes, vented-filter cigarettes, and European black-tobacco ciga-

Table 1.	Replicate	titration of	a known c	vanide solution '
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Run No.	μequiv. found
1	3.30
2	3.48
3	3.40
4	3.43
5	3.40
6	3.50
7	3.38
8	3.43
9	3.38
10	3.40

 Theoretical, 3.40 µequiv.; standard deviation, 0.055; relative standard deviation, 1.6%; recovery, 100.3%.

 
 Table 2.
 Reproducibility of coulometric and spectrophotometric methods for HCN in the smoke of a filter cigarette.

Method	µg HCN/cig. (average)	Standard deviation	Relative standard deviation (%)
Coulometric	270	14.3	5.31
Spectrophotometric	266	17.1	6.42

\* Ten determinations of two cigarettes per determination.

Table 3. Comparison of coulometric and spectrophotometric methods.

	μg HCN/cigarette		
Cigarette	Coulometric method	Spectrophoto- metric method	
Filter	270	276	
Kentucky 1R1 (non-filter)	376	379	
Molded-filter	155	152	
Non-filter	275	272	
Filter	270	270	
Vented-filter	89	92	
Black tobacco (filter)	238	246	
Vented-filter (low-TPM*)	25	30	

\* total particulate matter

rettes, were analyzed by coulometric and spectrophotometric methods (7). The results are shown in Table 3. The results obtained by the coulometric titration agreed

Figure 6. Effect of filter vents on HCN in cigarette smoke.



closely with the data obtained by the spectrophotometric method (7). Statistical treatment indicated that the data are not significantly different at the  $95 \,^{\circ}/_{0}$  confidence level. Since these original data were obtained, a new coulometer was constructed and the sensitivity of the indicator electrode was improved. The new instrument is more compact and easier to use than the older instrument.

In the various cigarettes analyzed as shown in Table 3, the vented-filter cigarettes gave much lower amount of HCN than the others. Thus ventilation is an effective means of lowering the HCN content of cigarette smoke.

Because of interest in vented-filter cigarettes, the effect of venting was examined more closely with filter cigarettes vented to provide 20, 40, and  $60^{\circ}/_{0}$  smoke dilution. A non-vented-filter cigarette was used as a control. The vents were situated 12.5 mm from the mouth end of a 20 mm filter. The cigarettes were smoked to within 3 mm of the overwrap. The results indicate that HCN was reduced more than expected from ventilation alone (Figure 6). The filters with  $20^{\circ}/_{0}$  ventilation reduced HCN content by  $27^{\circ}/_{0}$ , those with  $40^{\circ}/_{0}$  ventilation reduced it by  $86^{\circ}/_{0}$ .

The vents may affect gas-phase HCN in the smoke by increasing diffusion through the cigarette wrap or by decreasing the smoke velocity and enabling removal of more of the particulate-phase HCN by the filter. To determine which mechanism was responsible for reducing the HCN, additional vented cigarettes with 20, 40, and 60% ventilation were prepared and smoked. The cyanide delivered and the cyanide trapped by the filters were determined. The results (Figure 7) indicate that less HCN was trapped by the filters than was expected. The amount of HCN trapped on the non-vented filter was 54  $\mu$ g. The reduction due to ventilation was expected to correspond to the percentage ventilation. However, as shown, lower amounts than theorized were found. These data indicate that in addition to effecting air dilution, diffusion is a dominant mechanism by which HCN is reduced in the smoke of vented-filter cigarettes. Similar results were obtained by Norman (8).



Figure 7. Effect of vents on HCN retained by an acetate

# SUMMARY

We have described a method for determining the HCN delivered in whole cigarette smoke and in smoke condensate extracted from filters. The method is simple, rapid and precise. It eliminates many manual operations and is semi-automatic.

# ZUSAMMENFASSUNG

Es wird über eine Methode zur Bestimmung von Cyanwasserstoff (HCN) im Gesamtrauch der Cigarette und in dem aus dem Filter extrahierten Kondensat berichtet. Das Verfahren ist einfach und arbeitet schnell und genau. Es ist halbautomatisch und macht viele manuelle Analysenschritte überflüssig.

#### RÉSUMÉ

On décrit une méthode pour la détermination de l'acide cyanhydrique (HCN) dans la fumée totale de la cigarette et dans le condensat de fumée extrait du filtre. La méthode est simple, rapide et précise. Elle est semi-automatique et supprime plusieurs opérations manuelles.

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