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## Traces of Chlorinated Solvent in Coffee Samples Determined by Ion Selective Membrane Electrodes

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Caffeine is extracted from coffee with solvents like methylene chloride, dichloroethylene, or trichloroethylene, mixing continuously the coffee with solvent; the caffeine-free coffee, after extraction, is submitted to an evaporation process to eliminate the solvent.

In practice, traces of solvent are trapped with the coffee and it is known that these traces remain also during the roasting process, either as such, or forming other volatile compounds containing chlorine.

The determination of traces of solvents in the caffeine-free coffee is a problem not well solved for the difficulty of determination of microgram amounts of chlorine (1—4).

The procedure of analysis is generally the following: the coffee mixed with an equal amount of distilled water is introduced in a boiling flask with a reflux condenser and purified air is bubbled in. The air with volatile compounds and aqueous vapour passes in a quartz tube maintained at 900°—1000°C. The solvent at this temperature is decomposed and the gas, at the exit, bubbles in an absorbing solution of alkaline arsenite. Chlorine formed in the quartz tube is reduced by arsenite to chloride; this is determined by different methods.

*Hadorn* and *Suter* in an earlier work precipitate the chloride with silver, filtering on fritted disk the AgCl and reducing to metallic silver. The silver dissolved with HNO<sub>3</sub> was titrated with dithizon. After this work *Hadorn* suggested a potentiometric titration. To obtain a potential jump at the end point the solution must be acid, mixed with alcohol and at about 0°C for lowering the solubility product. The time necessary to perform the titration is quite long because of the slow equilibrium near the equivalent point. The precision of the titration (10—20 %) is quite low.

In this work a chloride specific ion electrode (5) has been used to evaluate its suitability for direct potentiometric determination of chloride in the absorbing alkaline arsenite solution, while the extraction procedure followed was that described by *Hadorn* and *Suter* (1—3).

Several modification to improve the original distillation apparatus for obtaining reliable results are also described in the text.

## Reagents

All water used was distilled and checked for the absence of chloride.

Absorbing solution:

weigh 3,75 g NaOH and 1,25 g  $\text{As}_2\text{O}_3$  of analytical reagent grade and dilute in a 250 ml flask with distilled water.

Acetic acid glacial 99,7 % reagent grade.

Chloride standard solution 0,0235 M:

weigh 1,752 g of KCl maintained at  $100^\circ\text{C}$  for 3 hours and dissolve in a 1000 ml flask with distilled water.

## Apparatus

In figure 1 the apparatus for volatilizing organic compounds and collecting chlorine is shown.

This apparatus was improved in respect to the original design to eliminate the water vapour condensation along the tubes that acted as absorbing material.

pH meter, AMEL Mod. 332 or similar instrument capable of scale expansion 0,2 mV/div.

Chloride ion selective electrode SENS ION Mod. 201 - Cl Amel Milano (Italy).

Reference electrode double junction: outer chamber filled with 1 M sodium nitrate solution.

Magnetic stirrer.

## Calibration curve

Obtain a calibration curve as follows:

mix 10 ml of absorbing solution with 1 ml of glacial acetic acid and 0,10, 0,50, 1,00, 2,00 and 5,00 ml of chloride standard solution and dilute with distilled water to 25 ml in a calibrated flask.

The concentrations of chloride solutions are as follows:

$9,41 \times 10^{-5}$ ,  $4,70 \times 10^{-4}$ ,  $9,41 \times 10^{-4}$ ,  $1,88 \times 10^{-3}$  and  $4,7 \times 10^{-3}$  corresponding respectively to 1, 5, 10, 20, 50 ppm of  $\text{CH}_2\text{Cl}_2$  in roasted coffee following the extraction procedure below described.

The chloride ion selective electrode and the reference electrode are put into the different solutions magnetically stirred and the potential value is recorded. The potential values are plotted conventionally on semilogarithmic paper.

In figure 2 the calibration curve thus obtained is shown.

This curve shows the limit of detection with use of chloride membrane electrode. The electrode follows the Nernst law until  $10^{-4}$  M because of the solubility product of the silver chloride as membrane material. Thus 1 ppm of  $\text{CH}_2\text{Cl}_2$  in roasted coffee is considered the limit of detection following the procedure outlined.

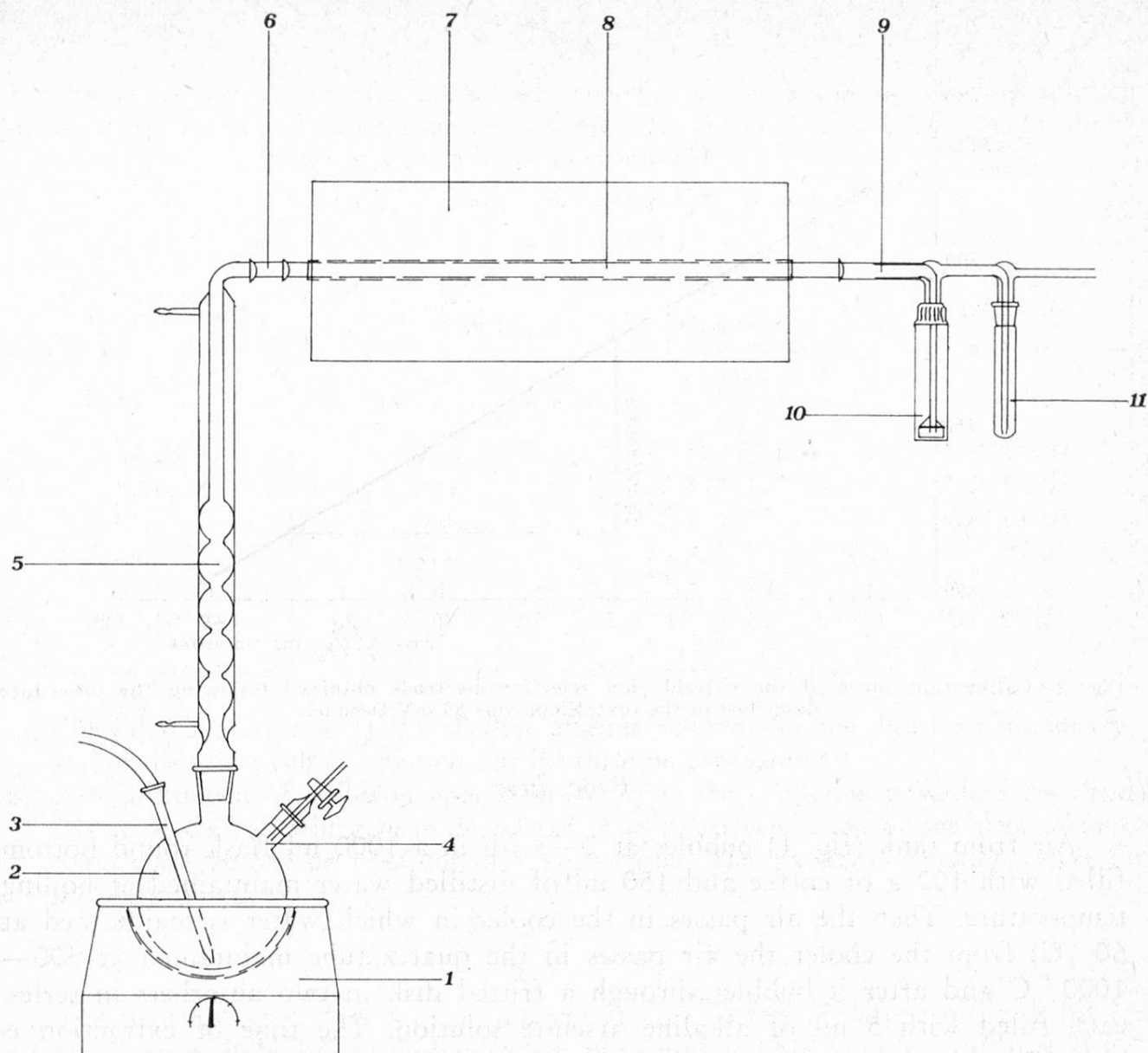


Fig. 1. Schematic view of the apparatus.

- 1 Heating mantle
- 2 1 l flask
- 3 Inlet for pure air tank
- 4 Valve
- 5 Reflux condenser at temperature of 60 °C in glass
- 6 Joint glass - quartz
- 7 Oven maintained at 900—1000 °C
- 8 Quartz tube  $\phi$  10 mm, length 50 cm
- 9 Joint quartz-glass
- 10 First absorbing unit: the gas bubbles in 7 ml of the alkaline arsenite solution, through a G2 fritted disk. The flow of the gas is regulated by flowmeter to 10—20 l/h.
- 11 Second absorbing unit: the gas bubbles in 3 ml of the alkaline arsenite solution through a fine glass capillary. This second unit was shown to be not necessary for general routine work.

The curve will be checked generally once a week because the electrodic response can be shifted along the ordinate axis with the aging of membrane electrode, with the variation of room temperature and with the variation of junction potential. Use of thermostat is not necessary if the analysis are performed in a ordinary chemical laboratory.



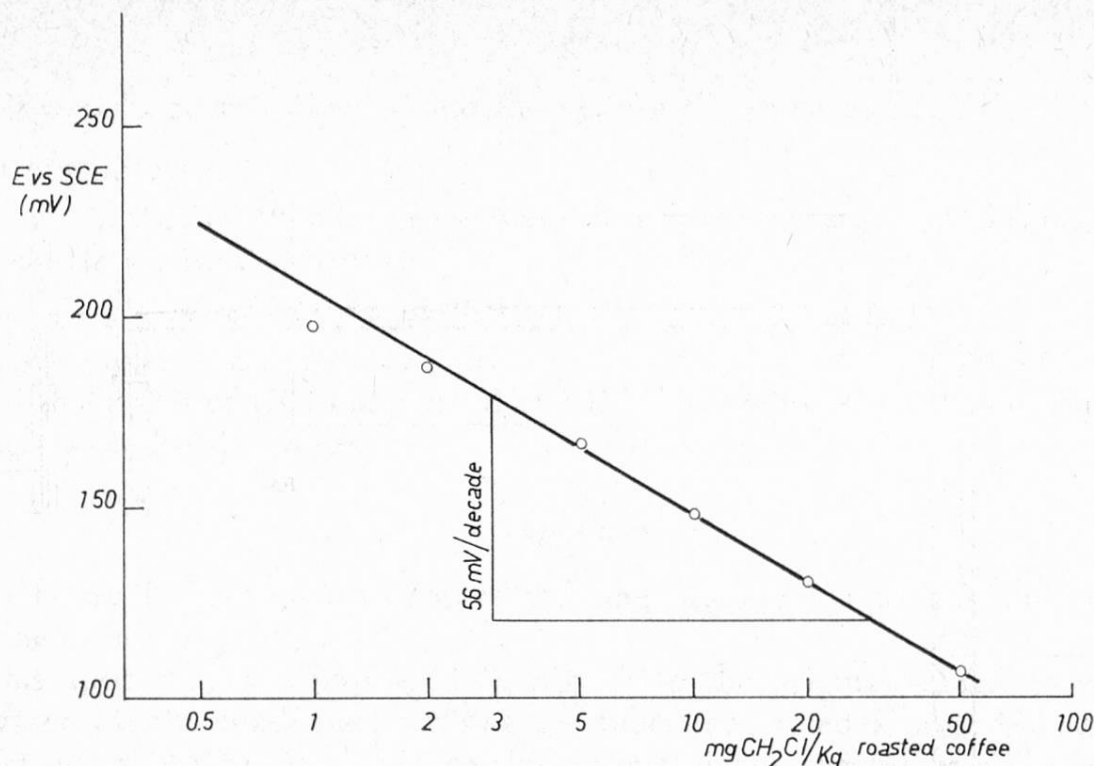


Fig. 2 Calibration curve of the chloride ion selective electrode obtained following the procedure described in the text. Slope was 56 mV/Decade.

### Procedure

Air from tank (fig. 1) bubbles at 2—3 l/h in a 1000 ml flask round bottom filled with 100 g of coffee and 150 ml of distilled water maintained at boiling temperature. Then the air passes in the cooler in which water is maintained at 60 °C; from the cooler the air passes in the quartz tube maintained at 900—1000 °C and after it bubbles through a fritted disk in two absorbers in series, each filled with 5 ml of alkaline arsenite solution. The time of extraction is about 3 hours.

After that time, open the stopcock 3 as in figure 1 and remove the absorber 10 and 11. The absorbing solution is poured in a 25 ml calibrated flask.

The absorbing unit should be carefully washed with distilled water and collected in a calibrated flask. Add 1 ml of glacial acetic acid and fill with distilled water up to the mark. Then shake the calibrated flask and analyze the sample with the chloride selective membrane electrode.

### Results and Discussion

The first point in this research has been to shown that the ion selective electrode procedure for the chloride determination in the collected alkaline solution is more practical and precise than the titration technique described by Hadorn and Suter (1—2).

Some results of determination of chloride in the alkaline arsenite solution obtained by the titration procedure and by direct potentiometry with the ion selective electrode are collected in table 1.

Table 1

Results of determination of chloride ion content of the absorbing alkaline solution obtained by argentometric titration in alcoholic medium (25 %) at 0 ° C and by direct potentiometry with a chloride selective electrode.

Vol. 25 ml. AgNO<sub>3</sub> conc. 0,01 M for the titration method.

Chloride <sup>a)</sup> concentration	Chloride <sup>b)</sup> content of coffee	Titration method Results <sup>c)</sup>	Direct Potentiometry Results <sup>c)</sup>
M	ppm	ppm	
$9,4 \cdot 10^{-5}$	1,00	$1,24 \pm 0,08$	$1,10 \pm 0,02$
$1,88 \cdot 10^{-4}$	2,00	$2,28 \pm 0,20$	$2,09 \pm 0,05$
$4,7 \cdot 10^{-4}$	5,00	$5,3 \pm 0,2$	$4,99 \pm 0,03$
$9,4 \cdot 10^{-4}$	10,0	$10,6 \pm 0,2$	$9,9 \pm 0,2$
$1,88 \cdot 10^{-3}$	20,0	$20,5 \pm 0,2$	$20,1 \pm 0,1$
$4,7 \cdot 10^{-3}$	50,0	$50,5 \pm 0,2$	$49,8 \pm 0,3$

- a) Chloride concentration of the alkaline arsenite solution for the direct potentiometry, and of the acid alcoholic solution, for the titration procedure.  
b) chloride content of coffee in ppm that, following the extraction procedure described (100 g of coffee), will give in 25 ml the chloride concentration of the first column.  
c) Results are quoted on ppm for easy comparison. The standard deviation refers to five determinations.

The titration procedure was performed at 0 ° C after acidification with nitric acid and with 25 % of alcohol with Ag wire and double junction calomel electrodes. An example of titration is shown in figure 3.

The mean time to perform such titration was about 30—40 minutes against the 2—3 minutes to obtain the response from the ion chloride selective electrode. The standard deviation is about the same in the two techniques for values in the range 10—50 ppm of CH<sub>2</sub>Cl<sub>2</sub>, but in the range 1—10 ppm the standard deviation for the titration method is higher because of the limit of applicability of the titration.

The precision of determination of chloride is quite poor in all ranges with the titration technique and this is probably due to chloride impurity content of alkaline arsenite. This impurity is cancelled out in the direct potentiometry because in this case the calibration curve is obtained with the same reagents (fig. 2).

We conclude that owing to the complexity of operation and of time consumed with the titration technique, the chloride selective electrode is recommended for routine work.

The second point of the research has been to test the all apparatus for extraction and subsequent determination with direct potentiometry to evaluate

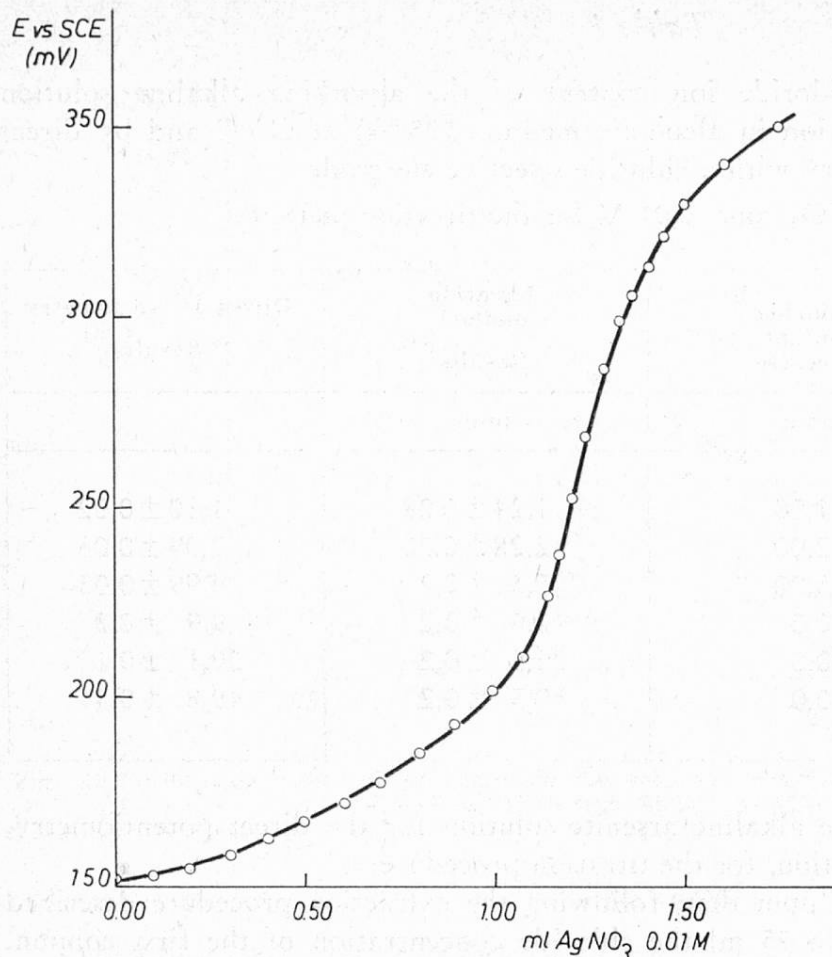


Fig. 3. Titration curve of 25 ml of the absorbing alkaline solution containing  $4.7 \times 10^{-4}$  M of chloride (5 ppm as coffee content); The solution was 25 % alcoholic, acidified with  $\text{HNO}_3$  and cooled to  $0^\circ\text{C}$  before titration.

the precision of the all procedure. In this phase of work we must modify the original apparatus and finally we obtain fairly good results in precision with the apparatus described in figure 1.

Note that the main differences has 1-using pure air from a tank; 2-eliminating the water vapour condensation in the apparatus that act as a trap for the gas; that is, the gradient of temperature must be positive from the reflux condenser (5 of fig. 1) and the quartz tube in the oven (8); 3- the absorbing unit has been prolonged as near as possible to the oven; in such way during the washing of the absorbing unit any liquid could be collected. The two last features were possible using ground joints made of quartz.

In table 2 several routine determinations on coffee roasted sample (100 g) are presented as example and the standard deviation obtained is higher than obtained in the table 1. This is obvious because of the complexity of the extraction process and of the losses of material. Nevertheless the all precision is acceptable for routine work in coffee practice.

### Summary

The determination of chlorinated solvent in coffee sample by use of a chloride ion selective membrane electrode is evaluated. The procedure is faster and more precise than



Table 2

Results obtained with different coffee sample in 0,15 l of distilled water

Sample (100 g)	Content of solvent residue ppm CH <sub>2</sub> Cl <sub>2</sub>	Mean ppm	Standard deviation ppm
A	2,6	2,4	0,5
	2,3		
	3,0		
	1,6		
B	3,3	4,5	1
	3,8		
	4,5		
	6,4		
C	6,6	7,0	1
	6,6		
	6,8		
	8,5		
D	32,0	47	10
	56,0		
	52,0		
	48,0		
E	36,0	31	6
	37,0		
	23,0		
	29,0		

the conventional potentiometric titration with silver ion and it is recommended for routine work.

### Résumé

Le dosage de résidus de solvants chlorés dans le café à l'aide d'une électrode sélective est étudié. La méthode est plus rapide et plus précise que le titrage potentiométrique conventionnel avec l'ion argent; elle est recommandée pour les dosages en série.

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