CYANIDE IN EFFLUENTS
Round Table: SOME ASPECTS OF THE CURRENT PROBLEM OF TANNING EFFLUENTS

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Moderator:

- **Lic. Patricia Casey** (Quality Manager at Curtiembres Fonseca and Vice President of AAQTIC's Board)

Panelists:

- **Eng. Maria Inés Iribarne** (Environment Manager at Curtiembre Hispano Argentina)
- **Dr. Carlos Gotelli** (Member of the National Academy of Pharmacy and Biochemistry -*Academia Nacional de Farmacia y Bioquímica*-; Member of the New York Academy of Sciences; Director of the National Center for Toxicological Research; and Consultant at the World Health Organization regarding heavy metals)
- **Horacio González** (Business Manager at Buckman)
- **Eng. Jorge Garda** (Environment Manager at Curtiembres Fonseca)
- **Eng. Martín Gelaf** (Technical Director at Curtiembre Hispano Argentina)

Main speaker: Eng. Martín Gelaf

Summary

The main purpose of the presentation is to show the findings made on an issue that worried the tanning industry in Argentina throughout 2010: the detection of cyanide in effluents from several tanneries.

Cyanide concentration values in tanning effluents have been measured and they turned out to be higher than the permitted 1 mg/l (1 ppm) according to the Standard Method (20th Edition) for total cyanide or 0.1mg/l of cyanide destructible by chlorination according to the Standard Method CN 4500 (paragraphs C and E). As a result, penalties such as closures have been applied.

This situation has no precedents in the national and international tanning industry and, to confirm it, some local authorities have been consulted and the opinion of foreign consultants has also been considered.

In view of such reality and knowing that tanners do not use cyanide in products for their processes, it has been decided that different alternatives should be researched on. These alternatives will be shared in this presentation.

It has been established that it is a complex issue, that conclusions are partial, and that further studies must be carried out. The purposes were:

- To understand the definition of cyanide pursuant to standards.
- To know how to prepare and preserve the samples to be analyzed.
- To understand the different laboratory methods to measure cyanide levels and challenge the values obtained and potential interferences that may appear.
- To analyze which chemical products may generate cyanide under certain special pH and temperature conditions, and presence of oxidants, among others.

There are a lot of doubts with respect to the foregoing issues since the different detection methods produced different cyanide values for the same effluent sample.

The most controversial chemical product which should be studied further is the use of the TCMTB fungicide (C9H6N2S3) which is the 2-(thiocyanomethyl) benzothiazole.

One of the manufacturers, a company named Buckman, has informed that the TCMTB molecule does not generate detectable levels of cyanide under regular conditions of application and treatment of tanning effluents, if the analytical methods are appropriate. The TCMTB chemical formula does not contain a labile cyanide group under industrial use conditions.
TCMTB is a product that decomposes at pH > 10 and temperatures > 120 °C; that is, the cyanide found was generated by the taking and preparation of the sample and the measurement method used.
Despite the remarks based on the need to treat TCMTB as interference in the analyses, many tanneries had to stop using TCMTB in their processes.
Another important issue is that work should be performed jointly with the Government Instrumentalities to know the adequate detection methods to be used, and to make sure that they are applied by qualified people, in contact with the tanneries' technical departments.
According to the information gathered in the inspected companies, the method used by the controlling authority is not the one stated by law, and the tests performed show that different methods lead to different results.
Sodium hypochlorite oxidation is the customary method for the elimination of cyanide from industrial effluents where cyanide salts are used (e.g. Electroplating). It has been confirmed that in the case of an effluent treated in the retanning process with limit values of 700 mg/l of DQO and 200mg/l of DBO the addition of sodium hypochlorite has caused an increase in the concentration of cyanide destructible by chlorination detected by laboratory method.

INTRODUCTION

In order to arrange and make the issues clear and to make this presentation more understandable, five basic topics have been developed:

1- Which are the cyanide types identified?
2- Which are the test techniques employed and what differences are there among them? Can they produce different results on a same sample?
3- What influence can the preservation of samples have and what interferences can be found?
4- What products employed in tannery can have a positive response to the cyanide determination test?
5- Which are the operations that may cause cyanide to occur in effluents?

DEVELOPMENT

1- Which are the cyanide types identified?

a- **Cyanide Ion** $[CN]^-$
b- **Inorganic cyanides:** inorganic compounds containing one or more cyanide groups bonded to a metal or ammonium ion, such as simple cyanide or metal-cyanide complexes.
c**- Organic cyanides:** organic **compounds** containing a functional cyanide group such as Cyanogenic Glucosides. Nitriles are also included.
d- **Free cyanide:** it is the bioavailable form and known for its toxic effect on organisms. It refers to the sum of **HCN and CN^-**
e- **Cyanides dissociable into weak acid:** they dissociate and release free cyanide when treated with weak acids (buffer solution of acetic acid/sodium acetate). They include weak metal-cyanide complexes (Zn, Cu, Ag, Cd, Hg, Ni).

f- ***Cyanide Amenable to Chlorination.*** Also known as Destructible by Chlorination. Cyanides that undergo dissociation and oxidation when exposed to chlorination under alkaline conditions = *Free Cyanide and Weak Acid Dissociable Metal-Cyanide Complexes.*

g- **Total Cyanide:** The sum of all cyanide inorganic forms that dissociate and release free cyanide when distilled under strongly acid conditions: they include **Free Cyanide** (HCN and CN^-), **Weak Acid Dissociable metal-cyanide complexes** (Zn, Cu, Ag, Cd, Hg, Ni) and **strong metal-cyanide complexes** (Fe, Co, Pt, Au). Some methods also consider that cyanides derived from organic compounds are included in this type.

h- Available cyanides: Those that dissociate and release free cyanide under ligand displacement reactions and are equivalent to the sum of free cyanides and the metal-cyanide complexes of Zn, Cu, Ag, Cd, Hg, Ni.

2 - Which are the test techniques employed and what differences are there among them?

The common features of the General Analysis Methods are the following:

a.- Formation of cyanide ion (CN^-) in the sample.
b.- Release and separation of the resulting hydrogen cyanide (HCN).
c.- Gathering and measurement of the resulting cyanide ion (CN^-).

A.- Formation of cyanide ion (CN^-) in the sample.

a.1- Heating under reflux in a strong acid environment.
a.2- UV digestion.

B1.- Release and separation of the resulting hydrogen cyanide (HCN).

b.1- Reflux distillation in a strong acid environment.
b.2- Short distillation in an acid environment.
b.3- Diffusion through a membrane.

Table No. 1 includes a summary of the described methods.

B2- Can they produce different results on a same sample?

Table No. 2 shows the differences on a same sample.
Analyses were carried out on tanning effluents at the Bayer Material Science LLC laboratory in Pittsburgh, Pennsylvania.

C.- Gathering and measurement of the resulting cyanide ion (CN^-).

HCN is gathered in an alkaline solution largely turning into a cyanide ion. Then, it may be measured by the following methods:

c.1- Tritation
c.2- Ion-selective electrode
c.3- Colorimetric method
c.4- Amperometric method

3 What influence can the preservation of samples have and what interferences can be found?

3a- Taking and preservation of sample

SM 4500 CN: preservation through alkalinization with NaOH and adding agents that stop the action of oxidizing substances.

ASTM D7365-09a: it recommends the addition of NaOH, *unless the cyanide concentration changes as a result of addition*. In the case of presence of oxidants, reducing agents must be added to mitigate its effect.

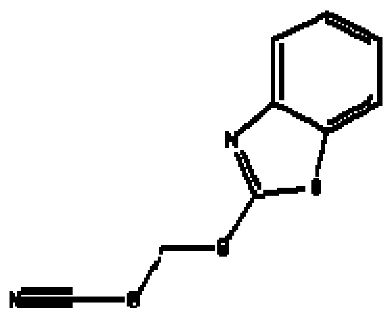
3b- The interferences that may be found are detailed in **Table No. 3.**

Data were taken from the respective Standards.

4 - What products employed in tannery can have a positive response to the cyanide determination test?

Tests performed on TCMTB solutions had a positive response with different cyanide analysis methods (without being considered an interference and previously isolated).

- TCMTB formula and data



- Molecular weight: 238.3
- Formula: C9H6N2S3
- CAS No. 21564-17-0
- The product is decomposed by preservation with caustic soda and the cyanide concentration detected is significantly increased. Values show an increase from 10 to 85 times when compared to the analysis without preservation.
- TCMTB was not treated as interference (thiocyanate).
- One of the manufacturers, Buckman, informs that the TCMTB molecule does not generate detectable levels of cyanide under the regular conditions of application and treatment of tanning effluents, if the analytical methods are appropriate. The TCMTB chemical formula does not contain a labile cyanide group under industrial use conditions.
- In the analyses, it must be treated as interference and previously eliminated.
- TCMTB is a product that decomposes at pH > 10 and temperatures > 120 °C; that is, the cyanide found was generated by the taking and preparation of the sample and the measurement method used (there is written documentation submitted by Buckman to the Chamber of Tanners).
- Despite the remarks based on the need to treat TCMTB as interference in the analyses, several tanneries had to stop using TCMTB in their processes.
- Other organic products (retanning based on dicyandiamide, melamine, organic fillers, acrylic resins, etc.) were analyzed using the same methods and no significant cyanide concentrations (concentration < x mg/l) were found.

- **Table No. 4** shows the products used in tanneries which may have a positive response to the cyanide determination: the TCMTB.
  Analyses were carried out at the Bayer Material Science LLC laboratory in Pittsburgh, Pennsylvania.

TCMTB has been diluted at 0.1% and the value found in the µg/l solution is equivalent to that of the raw liquid expressed in mg/l due to such dilution performed for this experiment.

The table shows once again that different techniques to determine the total cyanide produce different results on the same sample. With respect to the preservation influence: the table shows the result for available cyanide; the total cyanide was also analyzed, by standard 4500, and values from 10 to 45 times higher were obtained.

5- Which are the operations that may cause cyanide to occur in effluents?

- Over liquid effluent samples of a treatment plant of a tannery that unloads in a sewage area (limit DQO 700 mg/l and DBO 200 mg/l), and which uses hypochlorite for odor control, it has been shown that with increasing concentrations of **residual chlorine** increasing concentrations of cyanide were registered.
- Moreover, it was randomly found, over effluent samples which had had a negative response to cyanide, with the use of a semi-quantitative measurement kit, that an addition of sodium hypochlorite generated the presence of cyanide ions.
- The first hypothesis of this behavior is that some organic compound decomposes in the presence of hypochlorite generating cyanide ion, which goes against experience, since oxidation might produce stable and less toxic cyanate.

CONCLUSIONS

Based on the presentation and the questions and answers, conclusions may be grouped as follows:

A – Conclusions on the presentation:

- Free cyanide and weak metal complexes, if present in the effluent, could be responsible for the instantaneous toxic effect.
- Alkaline pH of effluent does not favor the release of free cyanide.
- There are different cyanide measurement methods which produce very different values for the same sample.
- Measurement techniques used for UV digestion are less aggressive and produce a minor decomposition of the original product.
- Colorimetric methods are more accurate than amperometric methods.
- Sample preservation methods affect the effluent cyanide results.
- There are a large number of interferences in the analytical methods to measure cyanides. Analytical techniques cannot be applied if interferences are not eliminated.
- Use of TCMTB had a positive response to cyanide with the different analysis methods.
- Samples preservation with sodium hydroxide containing TCMTB produced a great distortion in the values measured.

B – Conclusions on questions and answers

- Cyanide found as from TCMTB would be generated by the energy conditions under which the samples are treated (taking and method applied).
- It is shown that the method used by the controlling authority ACUMAR (Authority of Matanza-Riachuelo basin) is not the one stated by law, and tests performed show that different methods produce different results.

- Controlling authorities act in reliance on data obtained from specific facts and not from history.
- The 7 deaths occurred in a house in Avellaneda, in September 1993, due to hydrocyanic acid poisoning were caused by an improper practice performed by an operator who sent to a sewage with acid pH, an electroplated truck with concentrated cyanide (400 gr/liter) which released fatal hydrocyanic acid. A family died, as well as a medical team sent to help them.
- Cyanide levels detected in tanning effluents can never generate the foregoing.
- Mercury compounds used as weed killers in the past have been replaced with others such as TCMTB, which do not contain said metal and therefore no mercury should be found in the tanning effluents.
- In developed countries the maximum mass load sent to the effluent in the concentration area is established, thus avoiding high waste volumes.
- Sodium hypochlorite oxidation is the customary method for the elimination of cyanide in industrial effluents where cyanide salts are used (e.g. Electroplating). It has been confirmed that in the case of a treated effluent of a retanning process with limit values of 700 mg/l of DQO and 200mg/l of DBO the addition of sodium hypochlorite has caused an increase in the concentration of cyanide destructible by chlorination detected by laboratory method.
- The controlling authority ACUMAR has executed an agreement with the company AySA, Agua y Saneamientos Argentinos S.A., and the effluent analyses are performed at AySA's laboratories, which use the ISO 14403 method, which differs from the SM 4500 standard used by the majority of tanneries.

RECOMMENDATIONS

Recommendations derived from the presentation:

- It is essential that laboratories chosen by the controlling authorities use the same methods and have the same qualifications as the laboratories regularly used by companies for their controls.
- All control systems implemented by both the official and the private parties should work in a coordinated way so that the huge technical and economic effort made by the companies is not wasted and to make sure that their purifying plants work appropriately and comply with the regulations in force.
- A formal presentation should be submitted to authorities with respect to the research performed, with the details found.
- The addition of chlorine to the effluent should be studied since in an alkaline environment the cyanide oxidation into cyanates takes place, which is the most stable manner, thermodynamically speaking, and also much less polluting, even when it is a slow response in the absence of catalysts.
- All chemical products bought by tanneries should be accompanied by the respective material safety data sheets (MSDS) to guarantee that no prohibited products are added due to lack of knowledge.
- INTI leathers should be the entity that coordinates the research works to standardize the criteria among tanneries and controlling authorities.

TABLE No. 1 - Which are the test techniques employed and what differences exist among them?

	CN Formation*	HCN Separation	CN Measurement*
SM 4500.CN* CyE Total Cyanide	Extended heating in a strong acid environment	Distillation in a strong acid environment	Colorimetric
SM 4500.CN* CyE Destructible Cyanide	Extended heating in a strong acid environment	Distillation in a strong acid environment	Colorimetric
ISO 14403:2002 Total Cyanide	UV Digestion	Short distillation in an acid environment	Colorimetric
ISO 14403:2002 Destructible Cyanide	UV Digestion	Short distillation in an acid environment	Colorimetric
ASTM D7284-08 Total Cyanide	Heating in a strong acid environment	Gas Diffusion Membrane	Amperometric
ASTM D7511-09e2 Total Cyanide	UV Digestion	Gas Diffusion Membrane	Amperometric
ASTM D6888-09 Destructible Cyanide*	Displacement of Ligands Agents	Gas Diffusion Membrane	Amperometric

*ASTM D6888-09 standard considers the Cyanide Destructible by Chlorination as equivalent to Available Cyanide.

TABLE No. 2 - Can they produce different results on a same sample?

Results reported as Total CN^- in ug/L (ppb).

Test Method	Total Cyanide					
	Standard Methods 4500 CN C/E		D7284-08		D7511-09e2	
Description	Distillation / Colorimetry		Distillation / Amperometry		UV Digestion / Amperometry	
Analysis Date	08/16/10		08/16/10		08/13/10	
Sample	Observed Total CN^-, ug/L	% Recovery	Observed Total CN^-, ug/L	% Recovery	Observed Total CN^-, ug/L	% Recovery
Wastewater Sample A	25.6		35.5		57.3	
Wastewater Sample B	16.5		26.9		45.3	
Quality Control						
Wastewater A Matrix Spike	219	96.7	210	87.3	219	80.9
Wastewater A Matrix Spike Duplicate	222	98.2	220	92.3	218	80.4
Continuing Calibration Check	211	110	200	105	198	110
Laboratory Control Sample	220	220	208	208	195	195
Method Blank	<5		<2		<3	

Continuing Calibration Check = 200 ug/L KCN as CN^- (available and total cyanide methods).
Laboratory Control Sample = 200 ug/L $K_3Fe(CN)_6$ as CN^-.
Matrix Spike and Matrix Spike Duplicate = Wastewater A fortified 200 ug/L $K_3Fe(CN)_6$ as CN^-.
Method Blank = laboratory water.
Methods D7284-08 and SM 4500 CN C/E were distilled using MIDI Distillation, then analyzed with amperometry and colorimetry, respectively.

TABLE No. 3 - What influence can the preservation of samples have and what interferences can be found?

Method	Description	Measurement	Interferences
Total Cyanide	Automated UV	Colorimetric	Aldehydes Color Fatty Acids Mercury Nitrate Nitrite Oxidants Sulfides Turbidity Sulfur Compounds Thiocyanate
Total Cyanide	Manual Distillation with H_2SO_4 and $MgCl_2$	Amperometric	Aldehydes Carbonates Nitrite Nitrate Oxidants Sulfide Sulfur Compounds Thiocyanate
Total Cyanide	Manual Distillation with H_2SO_4 and $MgCl_2$	Manual or Automated Colorimetric	Aldehydes Carbonates Fatty Acids Nitrate Nitrite Oxidants Sugars Sulfide Sulfur Compounds Thiocyanate Color Turbidity

TABLE No. 4- What products employed in tannery can have a positive response to the cyanide determination test?

Results reported as CN^- observed in prepared solutions (ug/L or ppb) and as calculated CN^- in the original raw material samples (mg/Kg or ppm).

Test Method	Available Cyanide			Total Cyanide								
	D6888-09			Standard Methods 4500 CN C/E			D7284-08			D7511-09e2		
Description	Flow Injection / Amperometry			Distillation / Colorimetry			Distillation / Amperometry			UV Digestion / Amperometry		
Analysis Date	08/13/10			08/16/10			08/16/10			08/13/10		
Sample	Observed CN^- in Solution, ug/L	% Recovery	CN^- in Raw Material, mg/Kg	Observed CN^- in Solution, ug/L	% Recovery	CN^- in Raw Material, mg/Kg	Observed CN^- in Solution, ug/L	% Recovery	CN^- in Raw Material, mg/Kg	Observed CN^- in Solution, ug/L	% Recovery	CN^- in Raw Material, mg/Kg
TCMTB 30%, 0.1% solution in water	81.0		81.0	56.9		56.9	113		113	69.6		69.6
TCMTB 30%, 0.1% solution with NaOH	6940		6940									
Quality Control												
Continuing Calibration Check	201	95.5		211	110		200	105		198	110	
Laboratory Control Sample	99.2	99.2		220	220		208	208		195	195	
Method Blank	<2			<5			<2			<3		

TCMTB 30% sample was weighed into water at 0.1% (wt./vol); sample indicated "with NaOH" was diluted/preserved with NaOH solution, pH>12.
TCMTB 30%, 0.1% solution in NaOH result exceeded calibration curve for available cyanide; reported concentration is estimated.
Continuing Calibration Check = 200 ug/L KCN as CN^- (available and total cyanide methods).
Laboratory Control Sample = 100 ug/L KCN as CN^- (available cyanide); 200 ug/L $K_3Fe(CN)_6$ as CN^- (total cyanide methods).
Matrix Spike and Matrix Spike Duplicate = Wastewater A fortified with 200 ug/L KCN as CN^- (available cyanide); 200 ug/L $K_3Fe(CN)_6$ as CN^- (total cyanide methods).
Method Blank = laboratory water.
Methods D7284-08 and SM 4500 CN C/E were distilled using MIDI Distillation, then analyzed with amperometry and colorimetry, respectively.

Note by *Tecnología del Cuero*:
The performance of the round table was filmed by Estudio Melipal. The resulting the recorded material was transcribed by Tinta Roja.
The drafting committee rewrote that material, by way of a summary, not following the sequence of presentations, questions and answers.
The presentation of the most important issues was prioritized.
The main task was performed by Eng. José Barna.