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European lead standardisation—its relevance to users

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Abstract

The European lead industry, including users and producers, has agreed to prepare unique standards for lead products and analytical control methods. A technical committee (TC) was created in 1993 within the Comité Européen de Normalisation (CEN) under the identification code CEN-TC 306. In 1998, 10 standards were prepared and two standards are available. To illustrate the work done by the experts, the lead 99.97 definition is presented in detail. Harmonisation has its limits. A unique standard for general applications, common to several countries, cannot cover all the numerous specific demands from users but has to reflect progress in refining and testing, and changes in demand. Recently, product standardisation covers the terminology of used products. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

1.1. Why standardise?

Each nation in the single European market has its own standards for defining lead and lead products. The definitions are not equivalent between standards and harmonisation is necessary. Most of the national standards were published more than 10 years ago and the preparation of a unique standard integrates the performance of modern technology in lead refining and quality control. Demand from users has changed and modern standards have to take into consideration the recent changes.

2. European standardisation

2.1. Organisation

The lead and lead alloys technical committee (TC) was created in 1993 within the Comité Européen de Normalisation (CEN) under the reference CEN-TC 306. The general secretary is in charge of the French normalisation association, AFNOR. The CEN TC 306 is subdivided into working groups, WG. Each has to standardise in the field of a well-defined work item (Table 1).

WG1: Rationalisation of the various definitions of refined lead grades existing on the market.
WG2: Harmonisation of cable alloy definitions in cooperation with cable makers.
WG3: Definition of analytical methods adapted to modern equipment.
WG4: A unique lead sheet definition for the single European market.
WG5: Creation of lead oxide definitions.
WG6: Terminology for lead scraps.

The working group secretary is in charge of one nation. Experts are appointed by each country. They vote the group convenor.

2.2. A very recent target: used products

To respond to the CEN requirements, product standardisation also has to take used products and by-products into consideration. In June 1998, during the European annual meeting, the delegates decided to create a WG for used lead products. The item adopted after consultation with professional associations in each country concerns a European terminology. It will define the main used products containing lead to support intra-community trading and recycling activities.

Definitions will indicate the product origin, its traditional collection and recycling. The precise technical definition of used product will not be covered by this standard in order to avoid spending too much time obtaining the agreement from all the experts on complex definitions and control methods.

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Table 1
CEN TC 306 organisation subcommittee items and standards in project

Subcommittee	Item	Project number
WG1	Lead	pr EN 12659
WG2	Cable alloys	pr EN 12548
	Battery alloys	No project
WG3	Analysis:Sampling	pr EN 12402
WG3	Analysis. Optical emission spectrometry (OES)	pr ENV 12908
	Analysis by flame atomic absorption spectrometry (FAAS) or inductively coupled plasma optical emission spectrometry (ICP-OES) without separation of the lead matrix	
	Analysis by FAAS or by ICP-OES after separation of the lead matrix	
	Analysis by FAAS or by ICP-OES after separation by coprecipitation	
WG4	Lead sheet for roofing	pr EN 12588
WG5	Lead oxide	pr EN 13086
WG6	Scraps	

2.3. How it works: procedures and identification

Experts in each work group prepare a standard project to be submitted to the approval of the committee member by an internal vote: experts of each nation comment on the project. Consequently it is modified and then registered by CEN. The first two letters 'pr' indicate the project step. After translation into three languages, the project is submitted to public inquiry. Each nation votes. Then, after the CEN agreement, each national standardisation body publishes the standard in their national language. The designation includes the nationality of standardisation organisation and a common European reference. For example, DIN EN 12908 and NF EN 12908 identify the same standard for one analytical method. This standard has not yet been adopted and it has the specific status of an experimental project with the identification code: pr ENV 12908. It is available.

3. The European standard for lead grades: pr EN 12659

The European standard has to integrate specific definitions of each national standard in a common grade definition acceptable by each country. The definition has also to be relevant to the general and specific applications of lead. The standard integrates modern lead refining of secondary or primary materials. The definition takes into consideration recent progress in analysis and control [1].

To illustrate these items, the European Standard pr EN 12659 'Lead' will be compared with existing European standards and the ASTM B29–92 'Standard specification for refined lead'.

3.1. Grade definitions

The number of grades defined in national standards is different (Table 2).

Table 2
CEN TC 306-lead grades in comparison with existing standards

	Pr EN 12659	ASTM B29-92	BSI 334	DIN 1719	NF A55 105	UNE 37 201	UNI 3165
	Europe	U.S.A.	U.K.	Germany	France	Spain	Italy
99,995		■					
99,99	▒		■	■		■	■
99,985	▒			■	■	■	
99,97	▒	■		■	■	■	■
99,94	▒	■		■		■	■
99,90		■		■	■	■	
99,5					■		

Existing grades are indicated in grey areas.
99.94 is defined as 99.95 in UNE.
99.90 is defined as 99.91 in UNE.
AFNOR defines two grades for 99.97 and 99.9.

One single grade is specified in the United Kingdom (BSI334) where five grades are specified in Germany (DIN 1719) and Spain (UNE 37 201). In France (NF A 55 105) four grades are defined with two definitions for 99.97 and 99.9 grades to differentiate lead refined from primary or secondary materials. Four grades are defined in the recent American standard (ASTM B29–92). One grade, the 99.97, has a defined application in this standard. It is intended for lead acid battery applications.

The European standard pr EN12659 defines the four grades 99.990, 99.985, 99.970, and 99.940, under codification PB990R, PB985R, PB970R, and PB940R.

They are for general application and not defined for specific application. However, they may support definitions for specific uses. Cable alloys of standard pr EN 12548 are defined with reference to the grade definition of pr EN 12659.

3.2. A common industrial grade = lead 99.97% = PB970R

Experts have agreed not to differentiate grades by the origin of the material: treated, primary or secondary. For many years, lead production has integrated the recycling of used products. Modern equipment is adapted for treating both primary and secondary materials. The PB970R grade defines the 99.970%. The impurity definition illustrates the harmonisation between existing standards, integration of user demand and non-differentiation of material treated. (Table 3).

3.2.1. Silver

In EN 12659, Ag content of 0.0050% maximum is equivalent to the higher content accepted in the French standard NF A 55 105 under the grade 99.97 'Affiné' (refined). In other national standards, As content is limited to 0.0030% for DIN, UNI, ASTM and 0.02% for UNE. The EN definition is adapted to lead grade refined without desilverisation. National standards are adapted to specific production or local markets. Harmonisation integrates the result of recent research work into battery performance [2]. There is no clear evidence of the poisoning effect of silver on gas evolution for a limited content of 0.0050%, even if it is frequently limited to 0.0010% without real reasons [3].

3.2.2. Bismuth

The maximum content defined in pr EN 12659 for Bi is 0.0300%. It is in line with the existing AFNOR definition. In DIN, the limit is 0.027%. In other standards, content is limited to 0.0250%. All these definitions are adapted to non-debismuthised grades.

3.2.3. Copper

The content of 0.0030% maximum is less than the 0.0050% accepted by NF and more than the content accepted by other standards of 0.0015 or 0.0010%.

3.2.4. Ni, Cd, Sb, Sn, As

With less than 0.0010% each in EN project, they are at a content equivalent or lower than the content specified in other standards with the exception of As and Sn specified at very low level in NF A 55 105.

This impurity level takes into consideration progress in control and ensures a better reproducibility of material performance.

Table 3
CEN TC 306

	EN 12659 PB970R	NF A55 105 99.97 raffiné	NF A55 105 99.97 affiné	DIN 1719 Pb 99.97	UNI 3165 Pb 99.97	UNE 37-201 -89 Pb 3	ASTM B 29–92 refined pure lead (1)
Bi	0.0300	0.0250	0.0300	0.027	0.0250	0.02	0.025
Ag	0.0050	0.0010	0.0050	0.003	0.003	0.002	0.0025
Cu	0.0030	0.0010	0.0050	0.001	0.001	0.015	0.0010
Zn	0.0005	0.0010	0.0010	0.001	0.001	0.001	0.0005
Fe	N.S.	0.0010	0.0010	0.001	0.001	0.002	0.001
Ni	0.0010	N.S.	N.S.	N.S.	N.S.	N.S.	0.0002
Cd	0.0010	0.0010	0.0010	N.S.	N.S.	N.S.	N.S.
Sb	0.0010	N.S.	0.0025	0.001	0.001	0.0100	0.0005
Sn	0.0010	0.0003	0.0003	0.001	0.001	0.001	0.0005
As	0.0010	0.0001	0.0001	0.001	0.001	0.002	0.0005
As + Sb + Sn	N.S.	0.0005	N.S.	N.S.			N.S.
Others			low content		0.002 each	0.002	Te: 0.0001
Total impurities	0.030	N.S.	N.S.	0.03	0.03	0.03	N.S.
Lead min per difference	99.970	99.97	99.97	N.S.	N.S.	99.97	99.97

PB 970 R definition.
Comparison with existing standards.
Maximum impurity content is in percent.
N.S.: Unspecified.
(1) In ASTM standard this grade is intended for lead acid battery applications.

3.2.5. Nickel

Ni has not been specified in national European standards but only in ASTM. In specifying the Ni, experts take into consideration both the potential pollution due to scraps containing Ni and the poison effect of Ni in lead oxide preparations for crystal applications or lead acid batteries.

3.2.6. Zinc

Zn is specified at 0.0005% in EN, as in ASTM, when the specified limit in other standards is 0.0010% maximum. A limited content of zinc may provide users with a limited oxidability of liquid lead.

3.2.7. Iron

Fe is not specified in EN due to its low solubility in pure lead. This insolubility does not allow the preparation of reference materials for analysis. In these conditions, experts have preferred not to specify this element. Iron is frequently specified in comparison with sulphuric acid for batteries in which iron dissolves easily and possibly pollutes the battery.

3.2.8. Cadmium

Cd specified in EN and NF has not been specified in other standards. Cd is specified to guarantee clearly a limited content of lead regarding environment policies regulating the content in most applications and materials.

4. The use of pr EN 12659

4.1. The effect of the total amount of specified impurities

Specified impurities have to be lower than 0.030% in total. This limit determines the typical analysis or real composition of material produced with reference to the European standard. A typical analysis is the only result to compare with national standards. Two materials, for one 99.97 definition, can be produced depending on refining with or without desilverisation and analysis compared to existing definitions.

Table 4
Lead 99.970: content of typical analysis compared to maximum content of various standards

	EN 12659 PB970R	DIN 1719 Pb 99,97	ASTM B 29-92 Refined Pure Lead (1)	Typical Analysis with Bi Ag refining	Typical Analysis without Bi Ag refining
	% Max	% Max	% Max	%	%
Bi	0,0300	0,027	0,025	0,0250	0,0220
Ag	0,0050	0,003	0,0025	0,0008	0,0040
Cu	0,0030	0,001	0,0010	0,0003	0,0008
Zn	0,0005	0,001	0,0005	0,0001	0,0002
Fe	N.S.	0,001	0,001		
Ni	0,0010	N.S.	0,0002	0,0001	0,0002
Cd	0,0010	N.S.	N.S.	0,0001	0,0003
Sb	0,0010	0,001	0,0005	0,0002	0,0004
Sn	0,0010	0,001	0,0005	0,0002	0,0003
As	0,0010	0,001	0,0005	0,0002	0,0003
Others			Te : 0,0001		
Total	0,030	0,03	N.S.	0,0270	0,0285
Lead	99,970 Minimum	N.S.	99,97 Minimum	99,9730	99,9715

(1): In the ASTM standard, this grade is intended for lead acid battery applications.
Depending on refining operations, lead 99.97 is produced with or without debismuthising and desilvering operations.
When refining includes these operations, the 99.97 grade may refer to all standard definitions and even with ASTM refined pure lead for battery applications. When refining does not include desilvering and debismuthising, the grade 99.97 refers to pr EN 12659 and not to DIN 1719 or ASTM grade. Silver content, 40 g/t in this example, is too high compared to 25 g/t maximum required by ASTM B29–92 and 35 g/t by DIN. These differences have no effect on use.
In addition, Te is specified in ASTM and not in other standards.

Table 5
CEN TC 306, PB985R definition, comparison with existing standards

	Pr EN 12659 PB985R	NF A 55 105 99.985	DIN 1719 Pb 99.985	UNE 37-201-89 Pb-2
Bi	0.0150	0.0100	0.01	0.01
Ag	0.0025	0.0010	0.001	0.001
Cu	0.0010	0.0010	0.001	0.005
Zn	0.0002	0.0010	0.001	0.001
Fe	N.S.	0.0010	0.001	0.0015
Ni	0.0005		N.S.	N.S.
Cd	0.0002	0.0003	N.S.	N.S.
Sb	0.0005	0.0003	0.001	0.0040
Sn	0.0005	0.0003	0.001	0.001
As	0.0005	0.0001	0.001	0.0015
As + Sb + Sn	N.S.	0.0005	N.S.	0.0050
Others				0.0015
Total impurities	0.0150	N.S.	0.015	0.015
Lead min per difference	99.985	99.985	N.S.	99.985

Maximum content in percent.
N.S.: unspecified.
In UNI 3165 and ASTM B29–92. This grade (99.985) is not defined.

4.2. Typical analysis of lead 99.97 according to PB970R grade

In most of the standard definitions, the total sum of impurities is limited to a total amount. Consequently, in the typical analysis or real composition of the product, each impurity content is lower than specified.

To illustrate the total amount effect, the typical analysis of lead 99.970 refined with or without desilverisation operations is compared to the definitions of EN 12659, DIN, ASTM B29–92. (Table 4)

The typical analysis of lead, refined with desilverisation under the EN definition, applies to the DIN and AFNOR definition. With the exception of tellurium, it may conform to ASTM B29–92, refined pure lead.

For lead produced without desilverisation, the typical analysis does not comply with the actual DIN or ASTM. The typical value for silver of 0.0040% is in conformity with EN, when it is limited to 0.003% in DIN and 0.0025% in ASTM. In most applications, a silver content of 0.0025% or 0.0040% does not create differences and material produced under the EN definition would be acceptable even in battery applications.

Other impurities are at a very low content and give real progress in the quality of the material.

5. The 99.985 and 99.990 grades

These two grades are codified PB985R and PB990R in pr EN 12659.

Table 6
CEN TC 306, PB990R, comparison with existing standards

	EN 12659 PB990 R	BS 334 A lead	DIN 1719 Pb 99.99	UNI 3165 Pb 99.99	UNE 37-201 -89 Pb-1	ASTM B 29–92 99.995
Bi	0.0100	0.005	0.005	0.005	0.005	0.0015
Ag	0.0015	0.002	0.001	0.001	0.001	0.0010
Cu	0.0005	0.003	0.001	0.001	0.001	0.0010
Zn	0.0002	0.002	0.001	0.001	0.001	0.0005
Fe	N.S.	0.003	0.001	0.001	0.0015	0.0002
Ni	0.0002	0.001	N.S.	N.S.	N.S.	0.0002
Cd	0.0002	0.0005	N.S.	N.S.	N.S.	N.S.
Sb	0.0005	0.0005	0.001	0.001	0.0010	0.0005
Sn	0.0005	0.001	0.001	0.001	0.0005	0.0005
As	0.0005	0.005	0.001	0.001	0.001	0.0005
As + Sb + Sn	N.S.		N.S.	N.S.	0.0015	
Others		S: 0.0005		0.002	0.001	Te: 0.0001
Total impurities	0.010	0.01	0.01	0.01	0.010	
Lead min per difference	99.990	99.99	N.S.	N.S.	99.99	99.995

Maximum content in percent.
This grade 99.99 is not defined in AFNOR NF A 55–105.
For ASTM comparison is made with 99.995 due to unspecified 99.99.

The comparison of the definition with existing standards illustrates the harmonisation and evolution of the definition (Tables 5 and 6).

These two grades, with limited silver content of 0.0025% and 0.0015%, are suitable for the production of lead out of raw material with a limited silver content or lead refined with a desilverisation operation. Experts have noted an increase in the maximum silver content in comparison with the definitions of existing national standards limiting the silver content to 0.001% with the exception of BS.

The two grades also differ in Bi content at 0.0150 and 0.0100%. These values are higher than the national standard values, 0.01 or 0.005%, and provide clear evidence of the non-toxic effect of bismuth. With a limitation of the total amount of impurities, the bismuth content will be lower than specified by actual definitions.

Other impurities are specified at 0.0005% or even 0.0002% for Zn and Cd, taking into consideration progress in refining and control. They are specified at a lower level than actual national standards.

6. Non-specified impurities: Co, Cr, Se, Te

These elements have the reputation of poisoning battery performance [4] and experts have preferred not to specify them for several reasons.

- Co and Cr have a very limited solubility and the risk of dissolving in lead is limited.
- Selenium has to be limited to a very low content of 0.0001% and analytical control methods such as spectrometry of spark emission is not suitable.
- Tellurium is not included in the standard for the same reason as Selenium: There is no routine control method available under 0.0005%.

For these elements, a specific agreement has to be negotiated between supplier and purchaser including the definition of the analytical control method.

7. Conclusion

In mid 1998, the standardisation committee CEN TC 306, created in 1993, produced most of the standards for covering lead product definitions. Experts have defined grades as a compromise between existing national standards and, in addition, they have integrated progress in production, and demand evolution.

Standards in chemical analysis methods will be produced within the next 2 years and supported by reference materials.

When the standards have been adopted definitively, in approximately 1 year for lead grades, the national grades will no longer exist. Users will have to refer to CEN standards. For specific applications and in agreement with suppliers, users will continue to specify their own definition using European standards for supporting this specification.

Used products are now within the scope of the committee and a standard for scrap terminology will be prepared.

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