

Chapter 2

Inorganic Contaminants of Food as a Function of Packaging Features

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Abstract Metals are the most abundant group of chemical elements on the earth's crust and can be found in all foods. Some of them are essential to the diet, within certain specific tolerances, while others are present as contaminants and pose a risk to the human health. The knowledge of the risk by metal contamination in foodstuffs is an argument of great importance. Along the production chain, foods may come in contact with metals at different stages of the production process: parts of industrial plants, storage tanks, tools and mainly primary packaging. Some packaging materials are metallic; in other situations (plastics, etc.), metals are only one of components with a specific role. After an introduction on the international legislation, this chapter examines the main types of food containers—from metallic to plastic ones—considering the function of the metal, both as structural material or additive. For each material and packaging, factors affecting the related risk of contamination are analysed. Some case studies are examined referring to stainless steel, tinfoil, aluminium, plastics and innovative packaging. The chapter concludes with a critical review with relation to some examples of metal concentration found in preserved foods, with a particular focus on heavy metals.

Keywords Corrosion · Engineered nanomaterial · European food safety authority · European regulation · Metal contamination · Migration · Specific migration limit

Abbreviations

Al	Aluminium
As	Arsenic
b.w.	Body weight
Cd	Cadmium
Ca	Calcium
CDC	Centers for Disease Control and Prevention
Cr	Chromium
Co	Cobalt

Cu	Copper
ECCS	Electro-coated chromium steel
ENM	Engineered nanomaterial
EDI	Estimated daily intake
EFSA	European Food Safety Authority
EU	European Union
FAO	Food and Agriculture Organization
FACET	Flavourings, Additives and Food Contact materials Exposure Task
FCM	Food contact material
ICP-MS	Inductively coupled plasma—mass spectrometry
TOF-ICP-MS	Inductively coupled plasma-time of flight-mass spectrometry
Fe	Iron
JECFA	Joint FAO/WHO Expert Committee on Food Additives
Pb	Lead
LoQ	Limit of quantification
Li	Lithium
Mg	Magnesium
Hg	Mercury
DM	Ministerial Decree
Ni	Nickel
AFC	Panel on Food Additives, Flavourings, Processing Aids and Food Contact Materials
ppb	Part per billion
ICP-AES	Plasma atomic emission inductively coupled spectroscopy
PP-g-PAA	Polypropylene-grafted-poly(acrylic acid)
PE	Polyethylene
PTWI	Provisional tolerable weekly intake
RASFF	Rapid Alert System for Food and Feed
SML	Specific migration limit
SSICA	Stazione Sperimentale per l'Industria delle Conserve Alimentari
THQ	Target hazard quotient
Sn	Tin
TFS	Tin-free steel
Ti	Titanium
V	Vanadium
Zn	Zinc
WHO	World Health Organization

2.1 Introduction

Metals are the most abundant group of chemical elements on the earth's crust, and they are found in all foods. Some of these elements, such as iron, calcium, potassium and zinc, are present in nature and are considered essential when

speaking of human diet at least, within certain specific tolerances. On the other hand, metals, such as lead, cadmium, arsenic and mercury, may be detected in foods and other commodities as contaminants and pose serious risks to the human health because of different factors, including the known bioaccumulation. Table 2.1 shows main effects on the human health resulting from deficiency or excess of certain metals.

The knowledge of the contribution of certain metals in various food matrices is extremely important for different reasons, including nutritional purposes and the necessity of preventing contamination episodes by toxic metals. By a general viewpoint, the detection of metals in preserved foods can have three main causes:

- Presence in raw materials used in the preparation of preserved foods. Metallic elements may be naturally present in raw materials. On the other hand, the detection of metals may depend on environmental contamination
- Presence in food preparations before of the final packaging. The cause(s) can be originated on one or more of processing steps. Examples: contact with metal parts of processing plant (tubes, tanks, valves and electrodes)
- Contamination of preserved foods during packing and especially during storage steps.

Depending on the level of contamination, several corrective actions have to be put in place including (a) analyses of raw materials, (b) evaluation of production steps and (c) the examination of packaging and/or distribution processes.

Table 2.1 Main adverse health effects of certain metals

Metal	Deficiency	Surplus
Calcium	Bone deformities; osteoporosis	Cataract; stones cock; arteriosclerosis
Chromium	Glucose's metabolic disorders	Lung cancer
Cobalt	Anaemia	Heart problems
Iron	Anaemia; kinky hair syndrome (Menke's)	Cirrhosis; neuropathies; Wilson's disease
Cuprum	Anaemia	Primary and secondary haemochromatosis; haemosiderosis; cirrhosis
Litium	Depression	
Magnesium	Nervous disorders; weakness; stunted growth	Anaesthetic
Manganese	Skeletal deformities; gonads dysfunctions	
Kallium	Muscle cramps; muscle weakness; paralysis	Addison's disease
Selenium	Liver necrosis	Fluid restriction; high blood pressure
Sodium	Addison's disease; lack of appetite; apathy; muscle cramps	

2.2 Legislation

The presence of metals in foods is regulated through two series of laws relating to the final product on the one part and to packaging materials (containers) on the other side.

With reference to preserved and packaged food products, the Regulation (CE) No. 1881/2006 and subsequent updates, lastly the Reg. (UE) No. 420/2011 [1] and (UE) 488/2014 [2], set limits on the content of different toxic metals: lead (Pb), cadmium (Cd), mercury (Hg) and tin (Sn) in foods. In addition, the Reg. (CE) No. 333/2007 [3], modified from the Reg. (UE) 836/2011 [4], defines methods of sampling and analysis for the official control of Pb, Cd, Hg, inorganic Sn, 3-monochloropropane-1,2-diol and polycyclic aromatic hydrocarbons in foods.

With relation to food packaging materials, several European and national rules govern packaging and materials in contact with food. Actually, the matter of food packaging legislation in the European Union (EU) is extremely complex. Normally, the EU legislation on food packaging can be subdivided in two different groups:

- General rules, which concern all the materials. These norms define fundamental requirements for a food contact material or object
- Specific rules, with relation to individual materials. There are only some specific rules at the European level: the main of these legislations concerns substantially plastic materials, while other legislative documents are directly correlated with the control of ceramic materials and cellulose.

In general, three fundamental points have to be mainly considered as the pilasters of these rules:

- Composition requirements: compliance with the so-called positive lists
- Specific migration limits (SML)
- Prohibited materials.

The ‘General Framework Regulation’ for all FCM is the Regulation (EC) No. 1935/2004 [5].

On the other hand, it has to be observed that specific requirements for metals and alloys used in food contact materials and articles are not defined at present in the EU legislation.

In detail, the following EU Member States have specific legal provisions or official recommendations on metals for food contact applications: Austria, Finland, France, Germany, Greece, Netherlands, Norway and Sweden. These provisions cover mainly the transfer of heavy metals from metallic food contact articles into foodstuff. Italy is definitely the country with the largest number of specific regulations for individual materials. For this reason, the main Italian legislation for food packaging, the Ministerial Decree (DM) 21 March 1973 and subsequent updates (DM 18 April 2007 no. 76 on aluminium and DM 21 December 2010, no. 258 on stainless, now repealed by the D.M.11 November 2013, no. 140) is often cited in this text [6–8].

Table 2.2 Use of metals in the modern industry of food contact materials

Main function or industrial uses	Main applications
Structural material	Tinplate 'Tin-free Steel' (TFS) or 'Electro-coated Chromium Steel' (ECCS) Aluminium
Additives and processing aids	Fillers Stabilisers Dyes
Active packaging	Oxygen scavengers Gas barrier agents Antimicrobial agents Antioxydants
Nanomaterials	Nanocompounds (Ag, Ti, Zn)

This series of rules regulates the use of metals (Table 2.2) when used as the main and structurally basis of containers (tinplate cans are one of the main examples) or considered as additives for packaging materials and objects (fillers and pigments in plastics). There are not harmonised documents with relation to the use of stainless steel at present.

Anyway, Article 3 of the Regulation (EC) No. 1935/2004 is considered and applied when speaking of specific non-regulated materials [5]. In detail, Article 3 clearly states that materials and article for food contact applications are not allowed, under normal or foreseeable conditions of use, to transfer their constituents to food in quantities which could:

- Damage the human health
- Modify the composition of the packaged food in an unacceptable way
- Cause the deterioration of sensorial features of the packaged food.

Recently, a new Resolution on metals and alloys used in food contact materials and articles has been published in December 2013 with the aim of overcoming the lack of specific regulations materials in the EU [9].

With specific relation to health risks arising from consumer exposure to certain metal ions, the above-mentioned Resolution recommends the adoption of legislative actions and other measures to the Member States. Substantially, health hazards are defined with relation to the detection of metal ions when released to food from food contact metals and alloys during manufacture, storage, distribution and use. The Resolution provides detailed principles and guidelines in the annexed Technical Guide on Metals and Alloys used in food contact materials and articles (first edition). Above-mentioned documents have been prepared in cooperation with European experts in this field from national authorities, manufacturers and private testing laboratories.

Interestingly, this Resolution defines quality requirements for materials such as aluminium foil, kitchen utensils and coffee machines without specific EU limits. For example, the release of nickel should not exceed 0.14 mg/kg, while Pb should

not be released in amounts greater than 0.0043 mg/kg (this amount is intended as the detected concentration of metal ions in food).

In addition, detailed instructions on laboratory testing are described in the Guideline [9], with specific relation to analytical methods for migration testing of food contact materials and articles made from metals and alloy. Finally, the technical Guideline provides necessary advices with concern to the preparation of the Declaration of Compliance (Sect. 1.3) for metals and alloys used in food contact materials and articles. In detail, the list of structural metals includes the following elements:

- Aluminium (Al)
- Antimony
- Chromium (Cr)
- Cobalt (Co)
- Copper (Cu)
- Iron (Fe)
- Magnesium (Mg)
- Manganese
- Molybdenum
- Nickel (Ni)
- Silver
- Sn
- Titanium (Ti)
- Vanadium (V)
- Zinc (Zn).

It has to be also considered that other metal contaminants and impurities can be examined: this group includes arsenic, barium, beryllium (Be), Cd, Pb, lithium (Li), Hg, thallium, stainless steel and other alloys.

2.3 Analytical Methods

At present, official methods for the analysis of metal contaminants (traces) in food matrices are given as follows:

- Flame and graphite furnace atomic absorption spectroscopy and
- Plasma atomic emission inductively coupled spectroscopy (ICP-AES).

The ICP-AES ensures an excellent analytical sensitivity when coupled with a mass spectrometer. This system, the 'Inductively Coupled Plasma-Mass Spectrometry' (ICP-MS), can determine metal concentrations below 10 parts per billion (ppb). In addition, the new 'Inductively Coupled Plasma-Time Of Flight-Mass Spectrometry' (TOF-ICP-MS) system (Argon plasma) enables faster analyses and allows higher precision in the isotopic analysis.

Moreover, electro-analytical techniques have been developed considerably in recent years. These methods can guarantee high precision and analytical

sensitivity; the small size of necessary instruments will favour the transport even for in situ analysis.

Normally, analyses are carried out using spectroscopic techniques after the proper preparation of samples by treatment with acids. Recently, several works have proposed new methods for sample preparation and analysis with increased sensitivity and the reliable determination of trace toxic contaminants.

For example, the development of sensitive and reliable analytical techniques for the precise monitoring of lead in various foodstuffs has been reported [10]. In detail, the enrichment and separation procedure for lead has been proposed prior to its flame atomic absorption spectrometric determination [10]. In these conditions, a very low limit of detection of Pb has been reported: $0.36 \mu\text{g/l}$ (3σ , $n = 7$). According to researchers, the application of this method to the determination of trace lead in beer and tea drinks may be proposed [10].

Other techniques have been recently developed and validated with concern to the determination of As, Cd and Pb contents by means of quadrupole ICP-MS [11]. These metals, of big concern when speaking of the human health, can easily enter the food chain through the environment and/or as a consequence of food manufacturing processes. As a result, foodstuffs may be considered the main human exposure route to these chemical elements [11]. For these reasons, the European Food Safety Authority (EFSA) recommends the reduction of the exposure to Cd and Pb so as to protect especially vulnerable subgroups of population (e.g. infants). On this basis, the availability of precise, accurate and sensitive analytical methods for the reliable detection of low concentration values is a key point especially for official control laboratories.

According to researchers, the determination of As, Cd and Pb contents by means of quadrupole ICP-MS can allow following limit of quantification (LoQ) values: 6.2, 1.2 and $4.5 \mu\text{g/kg}$ for As, Cd and Pb, respectively, in strict accordance with requirements set in the Commission Regulation (EC) No. 333/2007 [11]. Pb and Co contamination in tap water and food samples can be also detected with a new procedure based on the formation of complexes of metal ions with 8-hydroxyquinolein in aqueous solution [12]. According to researchers, the preconcentration and separation of metals by solid-phase extraction (with paper filter) can be followed by spectrofluorimetric determination. Detection limits have been found to be 0.043 and $0.0219 \mu\text{g/l}$ (signal/noise = 3) for Pb(II) and Co(II) ions, respectively, [12]. The new methodology has obtained satisfactory results when speaking of the determination of trace amounts of Pb and Co in foods samples (milk powder, express coffee and cocoa powder) and tap waters from different regions of Argentina [12].

2.4 Metal Contamination and Toxicology

The toxicological risk evaluation, also in the case of metals, is based on two key factors in different situations, including also metallic contaminants: (a) the hazards of the migrating substance and (b) the correlated amount. Different factors have to

be taken into account: the nature and the composition of the material, the type and the composition of surfaces, the temperature and time of contact. In addition, the evaluation of the exposition of every single metal is crucial.

The 'Flavourings, Additives and Food Contact materials Exposure Task' (FACET) European project has given an important contribution in terms of the creation of a database containing information on levels of different food-related substances and corresponding food consumption data [13]. The covered packaging materials have been plastics (flexible and rigid materials), metal containers, light metal packaging, paper and board materials, as well as used adhesives and inks. This project has established a migration modelling framework for packaging materials into foods under real conditions of use. On these bases, the realistic estimation of substance concentrations for consumer exposure modelling has been obtained with the consequent creation of a reliable food intake database [13]. Generated data can provide exposure estimations using probabilistic models. It has to be also noted that the evaluation of exposure is expressed for individual consumers and various percentiles of different populations and subpopulations, when covered by national dietary surveys.

2.4.1 Aluminium

At present, there is no indication of any adverse health effects caused by released aluminium from packaging material, when speaking of packaged food products.

The Joint FAO/WHO Expert Committee on Food Additives (JEFCA) of the Food and Agriculture Organization (FAO) and the World Health Organization (WHO) has established a 'Provisional Tolerable Weekly Intake' (PTWI) of 1 mg/kg body weight (b.w.) for aluminium in 2006 [14]. This limit applies to all aluminium compounds in food, including additives. The EFSA has adopted the same PTWI in 2008 [15]. Subsequently, the European Commission (EC) has reviewed use levels and conditions of use for aluminium-containing food additives. The Commission Regulation (EU) No. 380/2012 [16] amends several provisions in Annex II to the Regulation (EC) No. 1333/2008 relating to aluminium and aluminium lakes; Annex II contains a positive list of additives approved for use in food in the EU and their permitted conditions of use.

2.4.2 Tin

At present, there is no indication of a chronic toxicity of Sn in humans because this element does not accumulate in the organism (traces in the bones > soft tissues). The acute toxicity of Sn is rather low: according to a recently published study, tin levels up to 267 mg/kg in foodstuff do not cause any harm to the health of adults. It should be noted that there is a great variation in the sensitivity of individuals to Sn. Different levels for chronic and acute toxicity of Sn could be established.

2.4.3 Lead

The human exposure to Pb causes a variety of health effects with particular relation to children. People are exposed to Pb through the air they breathe, through water and through food/ingestion. Toxic effects are usually due to long-term exposure. The Centers for Disease Control and Prevention (CDC) in the United States of America has defined 10 µg/dl of whole blood as the reference blood Pb level for adults [17]. This level is reduced when speaking of children: 5 µg/dl of blood [17]. On the other hand, the maximum limit for Pb in canned tomato paste is 1.0 mg/kg according to the Codex Standard 193-1995 [18].

2.4.4 Cadmium

Oral exposure to Cd may determine adverse effects on a number of human tissues, including also the immune system, and the cardiovascular system [19]. The intake of Cd from the diet is usually about 0.0004 mg/kg/day, roughly ten times lower than the typical amount needed to cause kidney damage by this route. With reference to this metal, the Codex Alimentarius Commission has defined a limit of 0.05 mg/kg [18].

2.4.5 Arsenicum

Inorganic As is well known as a notable human carcinogen; in addition, children can suffer other health problems in later life. Available data have shown that inorganic As causes cancer of the lung and urinary bladder, in addition to skin damages. There are no limits for As in most foods with relation to the USA, but the recognised standard value for drinking water is 10 ppb. With concern to the European viewpoint, the EFSA has recommended that the dietary exposure to inorganic As should be lowered in comparison with the JECFA PTWI of 15 µg/kg b.w. [20].

2.4.6 Rapid Alert System for Food and Feed

The current situation of food contamination in the EU can be reliably monitored by means of the 'Rapid Alert System for Food and Feed' (RASFF). This tool can be useful because of the possibility of exchanging rapidly information on measures taken to ensure food safety among the member States of the EU. Food contact materials (FCM) are included in the group of categorised products of interest for the RASFF. As an example, 516 episodes of alert have been notified in 2012 with relation to Italy only: 95 of these notifications have concerned FCM. By a general viewpoint, main causes of rejection appear to be the release of heavy metals and a high level of total migration.

2.5 Packaging Materials: Examples of Applications

2.5.1 *Stainless Steel and Glass*

Both stainless steels and glass for FCM production contain heavy metals, Ni, Cd and Pb: all these elements can migrate into foods. With relation to metal contamination in foods and the correlated risk management, the Italian legislation can be taken as a reference. In particular, the DM 21/03/73 [6] and subsequent updates include both regulatory compliance of the composition and SML. With exclusive reference to Italian norms, available maximum limits are 0.1 mg/kg for Cr and Ni, and 0.3 mg/kg for Pb. The migration of these metals is easily observed. For example, Table 2.3 shows several concentration values of these metals in tomato puree and lemon juice after 12 months of storage under nitrogen at room temperature: these determinations have been carried out by the Italian *Stazione Sperimentale per l'Industria delle Conserve Alimentari* (SSICA). Sampled foods have been stored in tanks manufactured in three different materials: stainless steel AISI 304, stainless steel AISI 316 and titanium. Results have shown that the overcoming of limit values for different metals is mainly dependent on the aggressiveness of the product, while the type of packaging material does not appear to have a similar influence. AISI 304 tanks appear to show the lower resistance to corrosion phenomena, in agreement with the literature and productive experiences.

2.5.2 *Metallic Cans and Tubes*

At present, the limit of migration for Sn is defined by European regulations (EC No. 242/2004 [21] and (EC) No. 1881/2006 [1] when speaking of tinfoil cans. In detail, Sn limits are established as a function of the kind of foodstuffs—from 50 to 200 mg/kg—as shown in Table 2.4. According to the EN 10333/2005 norm, the use of Sn is also foreseen with a minimum degree of purity of 99.85 % with the aim of reducing the content of heavy metals such as Pb [22] (maximum allowed concentration in tin coatings have to be lower than 0.01 %).

Moreover, the Italian DM 18 February 1984 sets a limit of 50 mg/kg for Fe in food products, while Pb is allowed between 0.2 and 3.0 mg/kg [23].

The corrosion process of tinfoil cans is very complex, depending on a large number of parameters. Briefly, it can be observed that corrosive phenomena occur mainly on tin coating in internally plain containers. On the other side, the risk of finding high concentrations of Fe in canned foods is greater when cans are internally lacquered.

This behaviour of tinfoil cans is exemplified in Table 2.5 and in Fig. 2.1. In particular, Fig. 2.1 shows that Sn limits are not exceeded even in the most unfavourable thermal condition.

Table 2.3 Detection of heavy metals in tomato puree and lemon juice after 12 months of storage under nitrogen at room temperature

Metal concentration (mg/kg)	Packaged food product (storage: 12 months of storage under nitrogen at room temperature)							
	Tomato puree (<i>passata</i>)			Lemon juice				
	Unpackaged	AISI 304	AISI 316	Titanium	Unpackaged	AISI 304	AISI 316	Titanium
Iron	3.32	3.78	3.70	2.94	0.70	65.3	5.42	2.66
Chromium	0.03	0.10	0.10	0.06	0.05	7.55	0.50	0.20
Nickel	<0.01	0.14	0.16	0.10	<0.01	5.50	0.16	0.14
Molybdenum	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Titanium	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

These foods have been stored in different tanks: the difference concerns the structural material of containers (stainless steel AISI 304, stainless steel AISI 316 and titanium). Apparently, the overcoming of limit values for different metals is mainly dependent on the aggressiveness of the product and on the type of material. AISI 304 tanks appear to show the lower resistance to corrosion phenomena

Table 2.4 Maximum allowed limits for inorganic tin, according to the Reg. (EC) No. 242/2004, Annex I, Sect. 6 [21]

Product	Maximum level (mg/kg wet weight)	Performance criteria for sampling	Performance criteria for methods of analysis
1. Canned foods other than beverages	200	Commission Directive 2004/16/EC	Commission Directive 2004/16/EC
2. Canned beverages, including fruit juices and vegetable juices	100	Commission Directive 2004/16/EC	Commission Directive 2004/16/EC
3. Canned foods for infants and young children, excluding dried and powdered products	50	Commission Directive 2004/16/EC	Commission Directive 2004/16/EC
3.1. Canned baby foods and processed cereal-based foods for infants and young children (1)	50	As above mentioned	As above mentioned
3.2. Canned infant formulae and follow-on formulae, including infant milk and follow-on milk (2)	50	As above mentioned	As above mentioned
3.3. Canned dietary foods for special medical purposes (3) intended specifically for infants	50	As above mentioned	As above mentioned

(1) Baby foods and processed cereal-based foods for infants and young children as defined in Article 1 of Directive 96/5/EC. Maximum level refers to the product as sold

(2) Infant formulae and follow-on formulae as defined in Article 1 of Directive 91/321/EEC. Maximum level refers to the product as sold

(3) Dietary foods for special medical purposes as defined in Article 1(2) of Commission Directive 1999/21/EC of 25 March 1999. Maximum level refers to the product as sold

Table 2.5 Tin contamination in peeled tomatoes

Capacity (kg)	Sn storage at 20 °C (mg/kg)	Sn storage at 37 °C (mg/kg)
0.5	112	147
1.0	122	132
3.0	92	121

Concentrations of Sn in plain cans of different capacity filled with peeled tomatoes after 9 months of storage (two different temperatures)

Fig. 2.1 Influence of storage temperatures on iron concentration in canned food products at different times. Metal cans are internally protected with white enamels

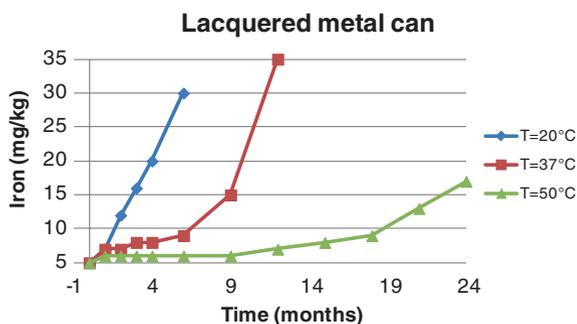


Table 2.6 Release of Al in canned tea products (different storage times, plain and lacquered aluminium cans)

Release of Al in different storage conditions	Plain sample	Lacquered sample
After 7 days, mg	3.25	
After 26 days, mg	7.69	
In steady-state conditions between 7 and 26 days		
mg	4.44	
mg/dm ² /day	1.17	
After 51 days		
mg		0.31
mg/dm ²		1.55

With relation to ‘Tin-Free Steel’ (TFS) or ‘Electro-coated Chromium Steel’ (ECCS) cans, the Italian reference is the DM No. 243 of 01st June 1988 [24]. According to this document, maximum allowed values for Cr in canned foods are 0.4 mg/kg (in four of the five samples) and 0.5 mg/kg (in the remaining sample). On the other hand, Fe cannot exceed 50 mg/kg.

With concern to Al, the Italian DM No. 76 of 18th April 2007 does not apply to aluminium materials and articles when coated with an organic film, such as cans and tubes [24]. On the other side, this legislation applies to all other uses of Al (e.g. foils and trays) and determines the degree of purity of Al and the composition of its alloys. At the European level, the following standards apply in relation to the chemical composition: EN 601, EN 602, EN 14287 and EN 13046/2000 norms [25–28]. Both materials, TFS and aluminium, are always protected with a lacquer when used for preserved foods; consequently, the migration of Cr and Al is reduced and there are not recognised limits. As an example, stringent corrosion tests (SSICA researches) on lacquered TFS samples in citric acid solutions (pH = 4) have shown the following values of Cr migration after 1 month of storage at 37 °C: 13.9–22.6–37.5–31.2–14.5 µg/kg. Anyway, the legally allowed maximum value of 400 µg/kg has not been exceeded. Migration values appear low in other situations concerning two pieces of aluminium cans for beverages with an organic coating (Table 2.6).

2.5.3 Regenerated Cellulose Films

The Commission Directive 2007/42/EC regulates materials and objects of regenerated cellulose film when intended to come into contact with foods [29].

With concern to these materials, metals have the function of additives: the quantity of each substance or group of substances must not exceed 2 mg/dm² of the uncoated film. According to the scientific literature, different molecules—oxides and hydroxides of Al, calcium (Ca), Mg and silicon; silicates and hydrated silicates of Al and Ca—are used. In addition, Ca, Mg, potassium and sodium are detectable because of the presence of related salts. As an example, Zn and Cr may be found up to 50–70 and 56–15 mg/kg, respectively, in different packaged foods after contact with recycled paper [7].

2.5.4 Plastic Materials

At the European level, the fundamental legislation for plastic materials is the Commission Regulation (EU) No. 10/2011: it determines SML or maximum usable amounts for each metal or metal salt included in the list [30]. In fact, metals are quite frequently used as components of plastic materials with different functions: dyes, fillers, pigments, antifouling, gas barrier agents, etc.

When speaking of plastic materials and metal components, a premise should be done because of the necessity of distinguishing between paints or enamels, adhesives or compound and plastic films.

First of all, titanium dioxide, zinc oxide or carbonate, aluminium oxide and barium sulphate are mainly used in paints as pigments. Titanium dioxide, barium sulphate, calcium carbonate and magnesium silicate or silicates of calcium and magnesium are used as inorganic fillers for the production of compounds for caps and cans.

Plastic films may easily contain similar substances: titanium dioxide, calcium carbonate and magnesium, silicates of calcium and magnesium, salts of cadmium, molybdenum, chromium, copper, gold and silver. Some of these additives—aluminium oxide, cobalt oxide, manganese oxide, calcium butyrate, calcium chloride, calcium hydroxide and calcium oxide—can be used without limits. On the opposite hand, the addition of certain metals may be restricted: for example, SML for antimony trioxide cannot exceed 0.04 mg/kg as antimony.

With relation to the Commission Regulation (EU) No. 10/2011, Annex II concerns the following SML restrictions for metals (analytical values are referred to foods or food simulants):

- Barium: 1 mg/kg
- Cobalt: 0.05 mg/kg
- Copper: 5 mg/kg
- Iron: 48 mg/kg
- Lithium: 0.6 mg/kg

- Manganese: 0.6 mg/kg
- Zinc: 25 mg/kg.

A useful and fast analytical technique to identify metals in a plastic film, compound or lacquer is the electronic scanning microscopy coupled to X-ray microanalysis. Figure 2.3 shows an example of application with relation to the analysis of a compound for caps (SSICA researches). The presence of barium sulphate has been detected in the area as shown in Fig. 2.2 (300× magnifications) as indicated by the X-ray spectrum (Fig. 2.3).

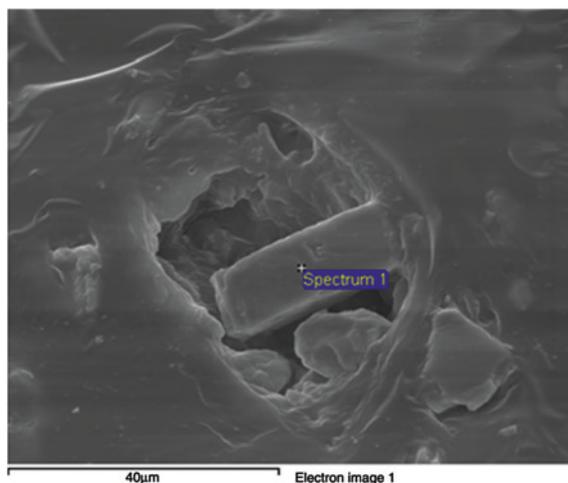


Fig. 2.2 Superficial deposition of barium sulphate on food contact caps (300× magnification). The detection of this sulphate has been confirmed by means of electronic scanning microscopy coupled to X-ray microanalysis (Fig. 2.3)

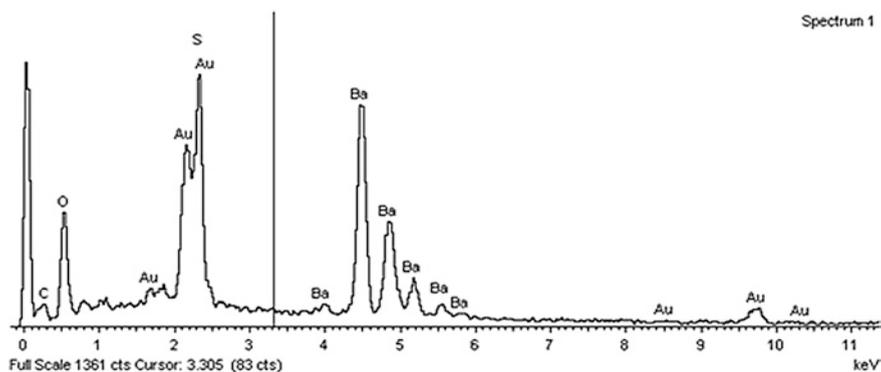


Fig. 2.3 Analytical detection (X-ray spectrum) of barium sulphate in a compound for food contact caps (Fig. 2.2). The analytical procedure concerns the use of electronic scanning microscopy coupled to X-ray microanalysis

2.5.5 Active and Intelligent Packaging: Nanotechnologies

The development of active packaging and the correlated use has progressively grown up in recent years: metals are used in this field with many functions, as briefly shown in Table 2.7. Active packaging instruments are ruled by the Regulation (EC) No. 450/2009 [31]. One of these devices, used in the packaging of sliced cooked hams, is shown in Fig. 2.4: the picture shows the section of a polyethylene (PE) film added with iron particles as oxygen scavenger (SSICA researches).

Actually, the sector of active packaging devices is notably diversified and in continuous evolution. Some examples can be reported here.

For instance, an innovative use of metals in plastic material has been recently discussed in 2014 [32]. Researchers have developed formulations of low-cost bio-based oxo-biodegradable PE/lignin hybrid polymeric composites prepared by

Table 2.7 Active packaging systems. A brief classification of main categories and correlated 'active' components

Active packaging categories	Chemical components
O ₂ scavengers	Clays
Humidity absorbers	Clays
Humidity regulators	Potassium chloride Sodium chloride
Carbon dioxide scavengers	Calcium chloride + sodium hydroxide Calcium chloride + potassium hydroxide
Antimicrobial agents	Titanium dioxide
Carbon dioxide emitters	Ferric carbonate + metal

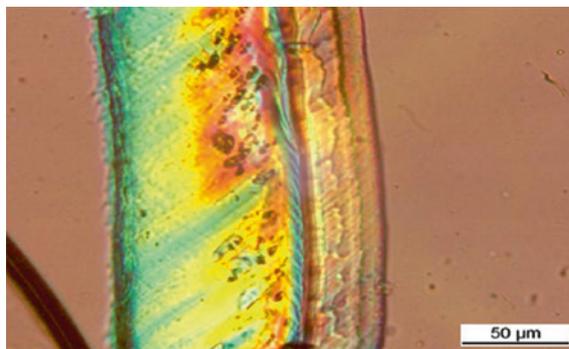


Fig. 2.4 This picture shows the image of a section of a polyethylene film added with iron particles as oxygen scavenger (food contact application: packaging of sliced cooked hams). The amount of iron-based oxygen scavenger is approximately 12 %

using ethylene vinyl acetate copolymer as compatibiliser and a transition metal salt as oxo-biodegradation promoter. The final aim has been the mitigation of the environmental burden caused by plastic waste items [32].

Another application [33] demonstrates the ability to tailor chelating activity of 'polypropylene-grafted-poly(acrylic acid)' (PP-g-PAA) with potential applications in active packaging. The development of iron chelating films prepared by photoinitiated graft polymerisation of acrylic acid on polypropylene can be very useful because Fe (and other transition metals) can enhance the oxidative degradation of lipids. In other words, active packaging labels with non-migratory metals can surely meet consumer demand for 'cleaner' labels. Substantially, the active PP-g-PAA-based material has been produced with a ligand (carboxylic acid)/metal (Fe^{2+}) binding ratio of $\sim 4\text{--}5$ [33].

In addition, nanotechnologies are used in food packaging: metal nanoparticles are used as tools for improving gas barriers, in particular oxygen. Nanoparticles may also act as nanosensors. At present, there is still no specific legislation. However, the evaluation of possible risks to the human health and to the environment should be done: unmetabolised nanoparticles can cause serious and incurable diseases to the human being. Recently, the EFSA has published the 'Guidance on risk assessment concerning potential risks arising from applications of nanoscience and nanotechnologies to food and feed' [34]. This document aims to discuss the characterisation, exposure scenarios and hazard identification for 'engineered nanomaterials' (ENM).

Basically, the use of nanoparticles in plastic packaging must be authorised by the EFSA in accordance with the Reg. (EU) No. 10/2011, Art. 9 (2): 'Substances in nanoform shall only be used if explicitly authorised and mentioned in the specifications in Annex I' [30]. For example, a peculiar restriction concerns titanium nitride (Annex I), in accordance with Annex I and an EFSA Opinion in 2012 [35]: 'No migration of titanium nitride nanoparticles. Only to be used in PET bottles up to 20 mg/kg. In the PET, the agglomerates have a diameter of 100–500 nm consisting of primary titanium nitride nanoparticles; primary particles have a diameter of approximately 20 nm'.

Because of the growing importance of nanotechnologies and possible consequences on the human health, the 'Scientific Network for Risk Assessment of Nanotechnologies in Food and Feed' (Nano Network) has been launched in February 2011. As a result, this organisation is expected to give an annual report on 'Risk Assessment of Nanotechnologies in Food and Feed' [34].

With concern to last scientific literature reviews, it has been recently outlined that the use of nanotechnology-derived food could be connected with the potency to lead to systemic toxicity [36]. This conclusion has been reported on the basis of existing data on the (potential) use of ENM in the food industry, including available information on toxicity profiles of commonly applied ENM such as metal (oxide) nanoparticles. In addition, researchers have also highlighted major gaps that need further research and regulation in this field [36].

From the analytical viewpoint, recent papers appear to highlight the importance of the quantitative amount of added amounts. For example, a new analytical

method based on ICP-MS has been developed with the aim of determining the migration of titanium from nano-titanium dioxide-PE films used for food packaging into food simulants under different temperature and migration time conditions [37]. In detail, researchers have found that the maximum migration amounts into 3 % (w/v) aqueous acetic acid were $12.1 \pm 0.2 \mu\text{g}/\text{kg}$ at 100 °C (the highest thermal values). On the other hand, maximum migration values of Ti were $2.1 \pm 0.1 \mu\text{g}/\text{kg}$ into 50 % (v/v) aqueous ethanol [37]. Briefly, researchers have revealed that the increase of additive contents in films may promote the migration of nanoparticles. In addition, nanoparticles appear to migrate via dissolution from the surface of films into the liquid phase (food simulant) [37].

2.6 Metals, Diet and Preserved Foods

With concern to the content of metals in preserved foods (restricted geographical areas or specific products), several papers are available at present. For example, a detailed study on the dietary exposure to several metals discusses available data with reference to the diet of adult British citizens in 1997 [38]. In detail, this research has demonstrated that the dietary exposure at the level of confidence of 97 % was 5.7, 0.024 and 1.9 mg/day per Al, Pb and Sn, respectively; in addition, detected results were below the official PTWI of 60, 0.21 and 120, respectively. It has been reported also [38] that the main sources of contamination were bread, cereals and fish (for Al), bread and nuts (for Pb) and finally tin canned vegetable products (for Sn).

Another work has concerned the evaluation of heavy metals contamination in Iranian canned tomato paste and tomato sauce (ketchup) [39] during the period 2010–2013. In summary, obtained results for Pb, Cd and As have been found lower than the limits of national and international standards in all samples. It has been reported that the average concentration of As was 62 ± 14 and $48 \pm 12 \text{ ng g}^{-1}$, while Cd values were below the LoQ in 7 % of tomato paste and 10 % of ketchup samples. Finally, Pb concentrations have been estimated below the LoQ in 75 % of tomato paste and 77 % of ketchup samples [39].

Similar works have concerned Cd, Pb and other metals in peculiar products of the *Maghreb*. For example, levels of Cd, Pb and Hg have been detected in fish from the Atlantic sea (Morocco) by the Moroccan Reference Laboratory as part of a specific monitoring program in 2014 [40]. Obtained results have confirmed that contamination amounts in muscles of fish correspond to the following values: 0.009–0.036, 0.013–0.114 and 0.049–0.194 $\mu\text{g}/\text{g}$ for Cd, Pb and Hg, respectively. As a consequence, researchers have concluded that fish and shellfish from southern areas of Morocco should not cause health problems for consumers [40]. Anyway, maximum residual levels have been found within the maximum residual levels prescribed by the EU.

With exclusive relation to fruits and vegetables consumed in Algeria, another paper has found that the estimated daily intake (EDI) and the target hazard

Table 2.8 Packaged foodstuffs in metallic containers and metal contamination: fish products

Fish products in lacquered metallic cans: metal contamination								
Fish product	Average values (mg/kg)				Maximum allowed admitted (mg/kg)			
	Lead	Cadmium	Mercury	Tin	Lead	Cadmium	Mercury	Tin
Tuna in olive oil	0.02	0.02	0.15	<3.0	0.30	0.05	1.0	200
Mackerel filet in olive oil	<0.03	<0.03	<0.1	<3.0	0.30	0.05	1.0	200

Table 2.9 Packaged foodstuffs in metallic containers and metal contamination: meat products

Meat products in lacquered metallic cans: metal contamination								
Meat product	Average values (mg/kg)				Maximum allowed concentration (mg/kg)			
	Lead	Cadmium	Mercury	Tin	Lead	Cadmium	Mercury	Tin
Meat of bovine	0.03	<0.03	(1)	<3.0	0.10	0.05	(2)	200
Turkey meat	0.04	<0.03	(1)	<3.0	0.10	0.05	(2)	200
Meat of chickens	0.03	<0.03	(1)	<3.0	0.10	0.05	(2)	200
Pork	0.04	<0.03	(1)	<3.0	0.10	0.05	(2)	200
Würstel	0.07	<0.03	(1)	<3.0	0.10	0.05	(2)	200
Medallions cattle	0.04	<0.03	(1)	<3.0	0.10	0.05	(2)	200

(1) This metal has not been researched in analysed samples

(2) There are not official maximum allowed concentration limits with concern to Hg in these products

quotient (THQ) may be defined below threshold values for Cu, Zn and Cr; on the other side, Pb values have been judged excessive (EDI: 15.66 $\mu\text{g}/\text{kg}$ b.w/day; THQ: 4.37), indicating an obvious health risk over a lifetime of exposure [41].

With concern to wines, trace **metal** contents have been studied for the first time in Italy [42] over the period 1995–2010. In summary, researchers have found that the decreasing use of pesticides and phytoiatric products has progressively determined the decrease of Cd and Cu residues in wines. At the same time, a significant decrease (about 74 %) has been observed for Pb from 1995 to 2010 [42], probably because of the diminution of Pb emissions in the atmosphere following the phasing out of metal from gasoline (in Italy since 2002).

The Italian SSICA has performed numerous analyses of the content of heavy metals in preserved foods. Tables 2.8, 2.9, 2.10, 2.11, 2.12, 2.13 and 2.14 show analytical results per different typologies of food product. Average results have been obtained with relation to different packs of the same lot.

In summary, the amount of Hg has been found below the detection limit of the instrument (<0.01 mg/kg) on all below-listed products:

- Guar gum (E412) and agar agar (E406)
- Food emulsifiers for mayonnaise, yogurt, ice cream, meat

Table 2.10 Packaged foodstuffs in metallic containers and metal contamination: cereals and cereal-based products

Cereals and cereal-based products in lacquered metallic cans: metal contamination						
Food product	Average values (mg/kg)			Maximum allowed concentration (mg/kg)		
	Lead	Cadmium	Tin	Lead	Cadmium	Tin
<i>Pasta</i>	0.03	<0.03	<3.0	0.2	0.02	200
Rice salad	0.03	<0.03	<3.0	0.2	0.02	200
Vegetable soup	0.04	<0.03	<3.0	0.2	0.02	200
<i>Tortellini</i> with meat sauce	<0.03	<0.03	<3.0	0.2	0.02	200
<i>Ravioli</i> with meat sauce	0.04	<0.03	<3.0	0.2	0.02	200

Table 2.11 Different packaged foodstuffs in metallic containers and metal contamination

Different canned foods and metal contamination								
	Average values (mg/kg)				Maximum allowed concentration (mg/kg)			
	Lead	Cadmium	Mercury	Tin	Lead	Cadmium	Mercury	Tin
<i>Fruit products in plain cans</i>								
Fruits salad	0.06	<0.03	–	39	0.10	0.05	(1)	200
<i>Milk powdered in aluminium tubes</i>								
Milk powder	0.01	<0.03	–	–	0.02	(1)	(1)	50
<i>Alcoholic beverages in glass bottles</i>								
Brandy	<0.01	<0.03	–	–	0.20	(1)	(1)	100

(1) There are not official maximum allowed concentration limits with concern to this metal for these food products

Table 2.12 Vegetable products and mercury contamination

Mercury contamination in canned vegetable products	
Commercialised food products	Average values \pm standard deviation (mg/kg)
Diced tomato in metallic cans	<0.1
Organic diced foods in metallic cans	<0.1
Tomato double paste in aluminium bags	<0.1
Tomato triple paste in plastic bags	<0.1
Dry mushrooms	2.54 \pm 1.42
Grinded dry mushrooms	4.69 \pm 1.94

- Food flavourings
- Ready products for mashed potatoes, croquettes and potato dumplings
- Minced and dried celery and carrots
- Red *pesto* sauce in glass jars
- Green *pesto* sauce in glass jars
- Cream of black olives in glass jars

Table 2.13 Fish products and mercury contamination

Mercury contamination in canned fish products		
Commercialised fish products	Average values \pm standard deviation (mg/kg)	Maximum allowed concentration (mg/kg)
Tuna olive oil in metallic cans	0.28 \pm 0.34	1.0
Tuna seed oil in metallic cans	0.46 \pm 0.10	1.0
Tuna olive oil in glass jars	0.43 \pm 0.36	1.0
Mackerel fillets olive oil in can	<0.1	0.5
Anchovies in glass jars	0.22	0.5
Clams in brine packed in glass jars	<0.1	0.5
Sardines in olive oil packed in glass jars	<0.1	0.5
Smoked salmon packed in plastic films	<0.1	0.5
Fresh cuttlefish packed in plastic films	<0.1	0.5
Fresh cod packed in plastic films	<0.1	0.5
<i>Pasta</i> with anchovies, packed in aluminium tubes	<0.1	0.5

Table 2.14 Semi-processed food products and metal contamination

Heavy metals (mg/kg) in semi-processed foods						
Semi-processed food products on the market	Arsenic	Cadmium	Lead	Cuprum	Zinc	Mercury
Smoked salmon	0.27	<0.01	0.11	<0.5	1.9	<0.10
Tuna in brine	0.10	<0.01	0.02	0.5	7.6	1.01
Cuttlefish	0.51	2.53	0.75	10.1	34	<0.10
Cod	0.21	<0.01	0.19	0.6	5.3	<0.10
Speck	<0.01	<0.01	0.02	1.0	30	<0.10
Sausage	0.02	<0.01	0.01	0.6	8.3	<0.10
Dry mushroom	0.19	0.62	0.61	18	24	1.14
Oregano	(1)	0.45	1.08	(1)	(1)	<0.10
Potato puree	0.01	0.04	0.04	1.5	3.2	<0.10
Peach in pieces	0.01	0.04	0.13	1.2	2.0	<0.10
Blueberries	0.02	0.02	0.05	<0.5	4.0	<0.10
Vegetables	0.02	0.05	0.16	<0.5	4.6	<0.10
Mozzarella cheese	<0.01	<0.01	0.06	<0.5	28	<0.10

(1) This metal has not been detected in analysed samples

- Dried and ground spinach in glass jars
- Ready sauce in glass jars
- Hot sauce in glass jars
- Tomato sauce with basil in glass jars
- Four-cheese Creamy in glass jars
- Minced Courgettes in glass jars

- Mashed potato in bags
- Apples-dried in bags
- Dried peaches in bags
- Dried cranberries in bags
- Diced and sliced organic carrots in glass jars
- Organic garlic paste in glass jars.

Generally, SSICA researchers have found lower values than the maximum allowed limits with the exception of two cans of tuna oil and with regard to Hg content. In particular, dried mushrooms are known to be a ‘critical’ product.

2.7 Conclusions

Metals have many different applications in food packaging (structural materials, additives, etc.). Current scientific papers report that metal amounts, especially heavy metals, usually comply with legal limits for preserved foodstuffs. Collected data seem to highlight that the influence of FPM is quite limited on condition that positive lists of composition and good manufacturing practices are fully implemented. For example, high concentrations may be due to anomalous corrosion process—this phenomenon still represents the exception—or contaminated raw materials, including also the well-known bioaccumulation. Even recent data on the content of heavy metals in food appear to confirm this conclusion.

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