Intergovernmental Forum on Chemical Safety
Global Partnerships for Chemical Safety

Contributing to the 2020 Goal

Heavy Metals in Food Packagings

The State of the Art

Prepared by: Professor Marcelo E. Conti
University of Rome, Italy

ROOM DOCUMENT

July 2008

HEAVY METALS IN FOOD PACKAGINGS

THE STATE OF THE ART[1]

MARCELO ENRIQUE CONTI

SPES - Development Studies Research Centre

Sapienza, Università di Roma, Via Del Castro Laurenziano 9, 00161 Roma, Italy.

Tel.: +39.06.49766516 – Fax: +39-064451566; e-mail: marcelo.conti@uniroma1.it

Food packaging materials have changed more in the past 15 years than in the previous 150 years, with a general, marked improvement of the quality, safety and nutritional content of packaged foods. The progress in understanding the toxicological relevance of the presence of heavy metals in food packaging is dependent primarily on the possibility of exactly determinating their content in selected matrices, and consequently on the further development of precise and accurate analytical methods.

In this context there are a number of possible sources of exposure to Pb and Cd via food packaging and food containers if not properly controlled. Heavy metals limitations stated in EU and US regulations can constitute a good starting point for similar guidelines in developing countries, where the information is very scarce. This is probably connected with the different packaging laws and also to problems inherent the analytical methods harmonization among these countries.

As little or no information is available on the situation in developing countries, this document provides an overview of the work and actions in the EU that may be of interest to other countries.

[1]Higher parts of this document were taken from: M.E. Conti (2007) Heavy metals in food packagings (Chapter 9), in: Mineral Components in Food, J. Nriagu and P. Szefer, Eds., CRC press, Boca Raton, Florida, USA, ISBN: 0849322340, 339-362.

In general, any migration of chemical substances from packaging to food is the result of a series of diffusion processes subjected to both thermodynamic and kinetic control.

The legislation in the area of food contact materials and articles is very complex and constantly in progress. Moreover, a strong scientific basis is necessary to support any decision making processes. The aim of EU directives is the harmonization of pre-existent national rules with the objective to avoid the legal barriers concerning a free circulation of foodstuffs and beverages.

The EU Framework Directive 89/109/EEC states that "food contact materials shall be safe and must not transfer constituents in quantities that could endanger human health or induce an unacceptable change in the foodstuffs composition". The Directive establish ten groups of materials and articles regulated in specific directives: (1) Plastics including varnishes and coatings; (2) Regenerated cellulose; (3) Elastomers and rubbers; (4) Paper and board; (5) Ceramic; (6) Glass; (7) Metals and alloys; (8) Wood, including cork; (9) Textile products; (10) Paraffin waxes and micro-crystalline waxes.

The Directive also establishes that all articles intended for food use shall be explicitly labelled ("for food use") or bear the corresponding symbol as stated by Directive 80/590/EEC (the symbol represents a glass and a fork).

There are specific directives for three groups of materials and articles: "Plastics", "Regenerated cellulose films", and "Ceramics". Besides, there are other pre-promulgation rules issued by Council of Europe (CoE) or by European Committee for Standardization (CEN). The CoE promulgates Resolutions and Guidelines that are not bind over for member states but they constitutes a common legal reference. The CEN issued an UE standards of reference and these will can be included in the EU directives.

The Commission Directive 2002/72/EC regulates the plastics packaging. This directive consolidates the Directive 90/128/EEC and its seven amendments. Generally these amendments modify the list of authorised substances.

The Directive 2002/72/EC establishes an overall migration limit (OML) of 60 mg (of substances)/kg (of foodstuff or food simulants) (10 mg/dm^2) for all substances migrating from a material into foodstuffs. The Directive presents also a positive list of authorised monomers and other starting substances with threshold limits on their use (and specific migration limits (SML) in food or food simulant) where applicable.

There are many substances of toxicological interest, restricted for plastic materials and articles intended to come into contact with foodstuffs. These are restricted trough the SML and QM (maximum permitted quantity of the residual substance in the material or article expressed as mg per dm^2 of the surface in contact with foodstuffs). SML “is applied to individual authorised substances and is fixed on the basis of the toxicological evaluation of the substance. The SML is generally established according to the acceptable daily intake (ADI) or the tolerable daily intake (TDI) set by the Scientific Committee on Food (SCF). To set the limit, it is assumed that, every day throughout his/her lifetime, a person of 60 kg eats 1 kg of food packed in plastics containing the relevant substance at the maximum permitted quantity”.

In the production process of thermoplastic polymers, such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyethylene terephtalate (PET), polycarbonate (PC), acrylonitrile-butadiene-styrene (ABS) and polyamide (PA), different catalysts may be used which can contain low levels of heavy metals. Generally, plastics used for food packaging contain low concentrations of metallic compounds. Lead and cadmium are sometimes present in plastic packaging articles. The sources for Cd and Pb are impurities originating from inorganic pigments and stabilisers.

However, the additives in plastics has a concentration less than 0.5 per cent by weight. Additives are present in high quantity of products, this make heavy metals quantification very difficult. Antioxidants can contain Ni, while thermal stabilizers can contain Ni, Pb and Sb.

Some metallic compounds are used as stabilizers of PVC. The PVC stabilizers contains Sn, cadmium in Ba/Cd carboxylates, that are the oldest PVC stabilizers. These stabilizers are substituted because of serious toxicological concern about cadmium. Ba/Cd stabilisers typically contains 1 to 15 % cadmium and usually constitute about 0.5 to 2.5 % of the final PVC compound. This PVC type is used, for instance, in water and drain pipes. Zinc in a liquid Ba/Zn stabilizer system that it is important because they are an alternative to cadmium-containing compounds in plasticized PVC. The Ca/Zn stearates and other carboxylates are strongly used for stabilizing non toxic PVC articles improving the manufacture of food contact packaging materials. Also lead compounds are strongly used as PVC stabilizers (i.e. primary lead salts, solid and liquid lead carboxylates). Most metal-free compounds used in the stabilization of PVC are costabilizers.

The EU Directive 94/62/EC (amended by 2004/12/EC) on Packaging and Packaging Waste sets out a maximum limit of 100 mg/kg for all Pb, Cd, Cr (VI), Cd and Hg in packaging materials. This limitation must be controlled for polymeric packaging materials and for calculate a possible heavy metal enrichment provoked by recycling processes of organic polymers.

Colorants are either pigments or dyes. Dyes are soluble at molecular level while pigments are insoluble in polymers. Pigments are particles whose dimension are comprised within the 0.01 - 1µm range size. It may generally be problematic to extract a list of colorants that represents the vast assortment of products that are used in food packaging applications. Nonetheless, pigments, dyes and inks also contribute, although less significantly, to the overall metal content.

There are two CoE Resolutions, one concerning the use of colorants in plastic materials and other concerns surface coatings that may contain colorants. Also there are a draft resolution on packaging inks and a draft technical document for the packaging ink raw materials.

Several types of inorganic pigments have been banned due to restrictions on the use of heavy metals like cadmium and lead. The CoE resolution AP (89) establish migration limits for antimony (<0.05 %), arsenic (<0.01 %), barium (<0.01 %), cadmium (<0.01 %), chromium (<0.1 %), lead (<0.01 %), mercury (<0.005 %) and selenium (<0.01 %). Also the use of Cr (VI) pigments for food contact use is discouraged.

There is no EU Directive for paper and board packaging. QM restriction limits are established for cadmium, lead and mercury by CoE Resolution AP (2002) on paper and board materials and articles intended to come into contact with foodstuffs. This document establish that paper and paper board are manufactured from cellulose-based natural fibres from bleached and unbleached fibre material. QM restriction quality limits (mg/dm^2 paper and board) are 0.002; 0.003; 0.002 for Cd, Pb and Hg respectively. The document establish also that SML restrictions, that will be reported in the “List of substances used in the manufacture of paper and board materials and articles intended to come into contact with foodstuffs”. At present, the SML restrictions can be tested (migration tests) using the conventional simulants reported in the plastic directives (82/711/EEC and its amendments). The conventional ratio for food contact conditions is 1 kg food to 6 dm^2 of paper.

Paper and board made from recycled fibres (fully or in part) should comply with the Resolution AP (2002) 1 restrictions and are subject to additional quality requirements to ensure their safety of use. These quality aspects are related to the presence in the feedstock of constituents of some substances such as additives, residues related to printing inks, adhesives or stickies, constituents arising from paper not used in food contact applications, etc.

Paper and paper derivatives are indeed one of the primary sources of food packaging all over the world. Paper packaging are more inexpensive and have high quality standards of safety of use.

As per plastic materials, toxicological effects of heavy metals generally occur at higher concentrations than expected in the most of packaging materials (ppm levels).

Few studies determine the total trace elements concentrations in the paper food packaging.

For instance Conti and Botrè (cited in Conti, 2007) reports heavy metals migration (3% acetic acid) tests in 7 samples of food packaging papers in the range: n.d. – 4.38; n.d. – 0.11; n.d. – 0.52 and 0.13 – 0.22 μg/g of Pb, Cd, total Cr and Cr VI respectively.

These studies show that substantial amount of heavy metals are present in some of the assayed samples. Metals that have been detected in higher concentrations are primarily lead and cadmium while the levels of chromium were in most samples below of detection limits. Cr VI was present at very low levels. It should be noted that where the product was made with 100% of virgin pulp heavy metals were never detected (e.g. ready to go pizza samples).

The de-inking process is often used in the recycling industry to enhance the quality of the recycled paper. The ink dispersion has a negative impact on the overall pulp brightness and, as above mentioned, inks can contain certain levels of heavy metals. The relevant increase of use of recycled fiber in wide variety of paper applications requires that de-inked pulp must meet always higher quality standards.

However, a few information regarding heavy metals in recycled fibre base materials and, to a greater extent, in paper food packagings, is available in the literature. On the other hand the several changes in EU laws and regulations in the past decade has probably influenced the very complex data interpretation obtained with many analytical methods. In view of this, it is also important to consider the difficulties of establish limits of toxicological concern.

The cooking process can induce migration of trace elements. Moreover, new saucepans on first use have the highest rates of chromium and nickel release.

Chromium or its compounds are also used in electroplating and in surface treatment of food cans. A ‘can’ is defined as an hermetically sealed container in which food is subjected to a ‘canning’ process that is heat treatment to increase shelf life. Most cans are made from tinplate that is a composite packaging material made up of a low carbon mild steel base. To prevent oxidation tinplate is ‘passivated’ with a thin layer with the same process above described.

Acidic foods can corrode the metal, thus cans are frequently coated internally with a lacquer that is mostly a polymerised resin on the tin surface. At present, in Europe, about 25,000 million food cans are produced every year; about 20% of these are unlacquered cans. The total worldwide production for food packaging is approximately 80,000 million cans. The performance of the lacquered food cans is greatly affected by the coating thickness.

In the past lead and cadmium pigments have been often used in ceramic glazes. The most important lead pigment is white lead. EU Directive 84/500/EEC strictly regulates lead and cadmium leaching from ceramic materials because their high toxicity. Colorants used in overglaze paints can contain pigments with lead, cadmium, zinc and other heavy metals. The FDA has established limits of 3 μg/ml for lead and 0.5 μg/ml cadmium when dinnerware is filled with 4% acetic acid for 24 hours at room temperature.

Automatic dishwashings and scrubbings seems not have great influence on release of lead from glazed ceramicware.

The EC directive 94/62 regulates tolerable concentration levels of Pb, Cd, Hg and Cr VI in glass packaging. In December 2003 guidelines on lead leaching from glass tableware into foodstuffs were given. This document established fundamental principles for lead leaching from glass hollowware and flatware and recommended to wash the products before first use because a high release of lead can occur only at the very first contact. Lead release decreased by nearly 20% after washing of unused crystal wine goblets. The weekly lead intake caused by lead extraction from tableware has been estimated in 35 µg/week if we assume a daily use of lead crystal stemware and a daily consumption of 5dL beverage.

The primary source of tin is associated with canned food; in the UK most of dietary intake of tin (94%) comes from canned fruit and vegetables. Unprocessed foodstuffs contain generally less than 1 ppm of tin. The PTWI for tin is 14 mg/kg body weight and recommended maximum permissible levels of tin in food are typically 150 mg/kg for canned beverages and 250 mg/kg (200 mg/kg for UK) in other canned foods. These levels of tin in foods can produce acute manifestations of gastric irritation in some individuals.

Also aluminium is mainly used in packaging materials such as saucepans, pressure cookers, foils, wrappers, frozen dinner trays, cans, roasting pans, etc. Usually, aluminium packaging materials are coated with an intermediate resin based coating. Thus, aluminium migration from coated food contact materials is negligible.