

## INFLUENCE OF TEMPERATURE AND IMMERSION TIME ON MIGRATION OF Cr, Mn AND Fe FROM METAL CANS

\*Kakalova M., Bekyarov G.,

University for Food Technologies – Plovdiv, Bulgaria

\*Kakalova Miroslava, [m.kakalova@gmail.com](mailto:m.kakalova@gmail.com)

**Abstract:** Temperature influence and immersion time over Cr, Mn and Fe migration from metal cans have been investigated during exposure to 3% acetic acid. Have been determined the linear regression between migration per unit contact area and duration time. The regression equations and corresponding correlation coefficients have been calculated at each of examined elements.

**Keywords:** migration of metals, food contact materials, food simulants, ICP-OES.

### Introduction

The sources of food contamination with metals are various: soil, chemicals used at fertilization, water used for food processing and cooking; equipment, containers and utensils used for food processing; packaging, storage and cooking.

The selection of a suitable packaging material for different application is a very important subject. In view of toxicological effect at component migration from packages into foods, which turns to crucial problem. Food packaging can interact with the foodstuff by diffusioncontrolled processes, which mainly depends on chemical properties of the food contact material, and the foodstuff, packaging temperatures, during heat treatment and storage, exposure to light, and storage time of the product [3, 4, 5, 6, 7, 8]. This interaction leads to the need of strict control of released compounds from the packaging towards the food.

Corresponding of migration from food contact materials with restrictions is commonly tested by simulation with standardized procedures. Simulant B, 3% acetic acid, is used

for simulating sour foods. EU Directive 97/48/EC, the 2<sup>nd</sup> amendment of Directive 82/711/EEC, specifies the test conditions: if the product is pasteurized or sterilized, these conditions should reproduced migration during long-term storage that simulated by 10 days at 40<sup>o</sup> C [2].

Current EC harmonised legislation specifies limits concerning the migration of Pb and Cd into 4% acetic acid when the test are carried out in ceramic and glass materials. No limits exist for any other metal ions for migration from metal packaging, intended for food contact. They are a subject of national legislation [1, 12].

The aim of this study is to investigate the influence of temperature and immersion time over the Cr, Mn, and Fe migration rates from metal cans exposed to 3% acetic acid.

### Experimental

**Test materials:** Four type commercial metal cans purchased in triplicate for the purpose of this study. All made from the same bulk material but with different capacity – C<sub>1</sub> (160 cm<sup>3</sup>), C<sub>2</sub> (180 cm<sup>3</sup>), C<sub>3</sub> (600 cm<sup>3</sup>) and C<sub>4</sub> (1000 cm<sup>3</sup>). All test packaging were washed carefully with a commercial detergent, rinsed with distilled water and dried in a desiccator at 100<sup>o</sup>C.

**Migration test:** After washing each of the all metal packaging were exposed in to 3% (v/v) acetic acid for a period of 240 hours (10 days) at 40<sup>o</sup> C in thermostatic chamber with controlled temperature and pressure. With purpose to be calculated the migration per unit contacting area and to per unit mass into acid it have been placed volume of acetic acid corresponding to the each volume of cans. Following the exposure the acid leachates were thoroughly mixed and a sub-sample was submitted after 24, 48, 96 and 240 hours.

**Determination of acetic acid leachates:** The acetic acid extracts were examined with ICP-OES Spectro Analytical Instrument – Modula. The contents of Cr, Mn and Fe were respectively determined at the working wavelengths 283.56 nm, 257.61 nm and 259.94 nm. The instrument conditions are as follow: E = 1200 W, Nebulizer gas – 26 bar, Coolant gas – 42 bar; Auxiliary gas – 26 bar. The working standard solutions with concentration of 0.1 ppm, 0.5 ppm, 2 ppm, 10 ppm and 50 ppm were prepared from IV multielement standard solution 1000 mg/L – Merck Germany and diluted to appropriate volume with 3% (v/v) acetic acid.

The quantity of each metal released (mg/dm<sup>2</sup>) was estimated using the formula:

$$M = \frac{C \cdot V}{S}$$

Where: M is a migration of an element in mg/dm<sup>2</sup>;

C – Concentration of an element in ppm (mg/dm<sup>3</sup>);

V – Volume of the 3% acetic acid in dm<sup>3</sup>;

S – Surface contact area in dm<sup>2</sup>.

The total amount of each metal released (mg) was calculated.

All experiments were carried out in threefold repetition and mean values with the respective error are presented in the figures below.

### Results and discussion

The obtained results show that a correlation exists between the element migration (expressed as mg/dm<sup>2</sup> and mg) and the immersion time of the tests. The results are shown in figures 1, 2 and 3. The equations are with coordinates: x - immersion time in hours and y – migration of the elements. The obtained linear functions in all cases have correlation coefficient close to 1. There was no observed zone of saturation up to 240 hours, suggesting an increasing migration after tenth day. This conclusion does not contradict the data in the literature referred [9, 10, 11].

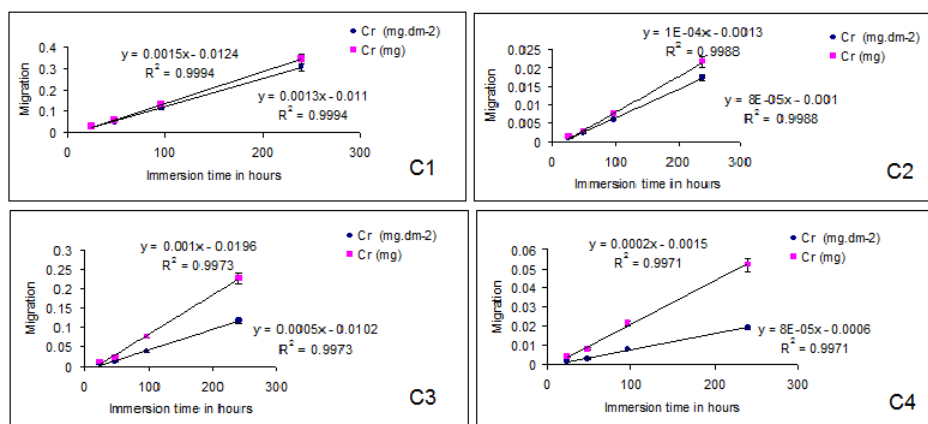


Fig. 1. Migration of Cr (mg/dm<sup>2</sup>) and the total concentration (mg) in metal packaging C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> depending of immersion time.

Figure 1 shows that from a square decimetre of contact area for an hour the rates of Cr migration are different for examined packaging. The highest value is observed for metal cans C<sub>1</sub> – 0.0013 mg/dm<sup>2</sup>, following of metal packaging C<sub>3</sub> – 0.0005 mg/dm<sup>2</sup> i.e. 3 times lower compared with C<sub>1</sub>. The metal migration rate for metal cans C<sub>2</sub> and C<sub>4</sub> is 0.00008 mg/dm<sup>2</sup> i.e. 16 times lower than the migration rate of C<sub>1</sub>. The differences in migration rates can be said is due to the processing technology used.

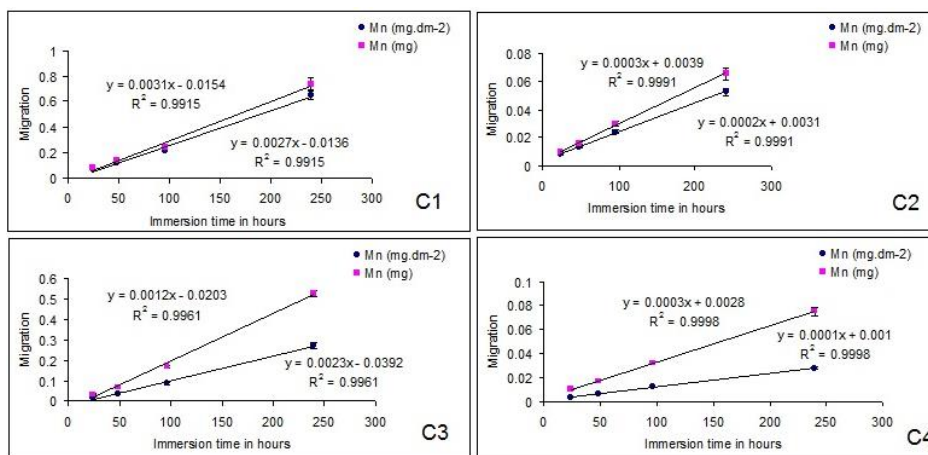
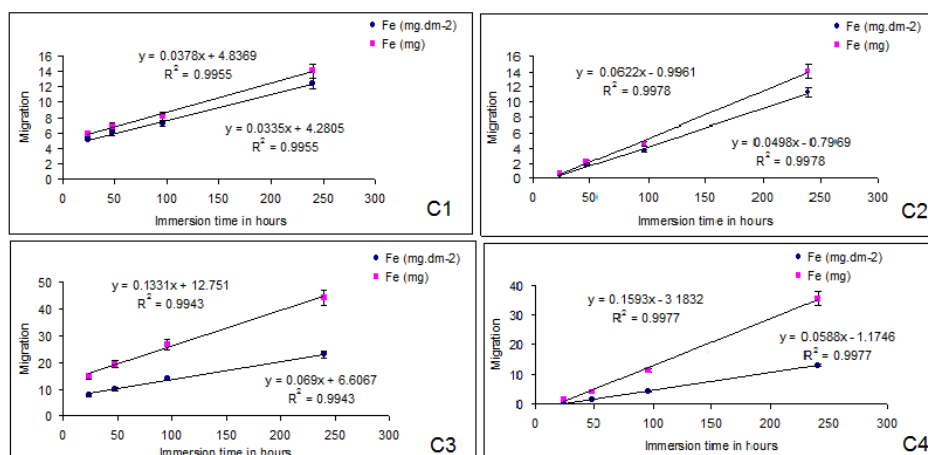


Fig. 2. Migration of Mn (mg/dm<sup>2</sup>) and the total concentration (mg) in metal packaging C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> depending of immersion time.

The results illustrated in figure 2 show that from one square decimeter of contact surface for an hour Mn migrates with the greatest rates from packaging C<sub>1</sub>-0,0027 mg/dm<sup>2</sup>, next is C<sub>3</sub> - 0,0012 mg/dm<sup>2</sup>. In type C<sub>2</sub> and C<sub>4</sub> rates of Mn migration are comparable - 0.0002 and 0,0001 mg/dm<sup>2</sup>.



**Fig. 3.** Migration of Fe (mg/dm<sup>2</sup>) and the total concentration (mg) in metal packaging C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> depending of immersion time.

Unlike Cr, Mn the migration rates of Fe increased in the first 24 hours for metal cans C<sub>1</sub> and C<sub>3</sub> series. After first 24 hour they increased linearly in the range of 24 to 240 hours. For C<sub>1</sub> the migration rate is 0.0335 mg/dm<sup>2</sup> and for C<sub>3</sub> - 0.069 mg/dm<sup>2</sup>. These results allow us to make a conclusion, that when determining the migration of Fe with procedures shorter than 24 hours can be leads misleading high values for this element.

#### Conclusion:

The migration of Cr and Mn increases in linearly compliance to the duration time of the test procedure.

The migration gradient of Fe into first 24 hour significantly exceeds than those obtained in the range of 24 to 240 hours. The duration time of test procedure for migration of Fe should not be less than 24 hours.

As can be seen the migration levels of Cr, Mn and Fe are different for the tested metal cans. The highest value was observed for Fe, followed by Mn and Cr.

#### References:

1. Barnes, K., Sinclair, R., Watson, D., (2007) Chemical migration and food contact materials, Woodhead Publishing Limited, Cambridge, England
2. Commission Directive 97/48/EC of 29 July 1997 amending for the second time Council Directive 82/711/EEC laying down the basic rules necessary for testing migration of the constituents of plastic materials and articles intended to come into contact with foodstuffs.
3. Conti, M., Botre, F., (1997) The content of heavy metals in food packaging paper: an atomic absorption spectroscopy investigation, Food Control, 8 (3), 131 – 136
4. Fankhauser-Noti, A., Fiselier, K., Biedermann-Brem, S., Grob, K.(2005). Epoxidized Soy Bean Oil (ESBO) migrating from the gaskets of lids into food packed in glass jars: Analysis by on-line liquid chromatography-gas chromatography (LC-GC). Journal of Chromatography A, 1082, 214–219

5. Fankhauser-Noti, A., Grob, K., (2006). Migration of plasticizers from PVC gaskets of lids for glass jars into oily foods: Amount of gasket material in food contact, proportion of plasticizer migrating into food and compliance testing by simulation. *Trends in Food Science and Technology*, 17, 105-112
6. Itodo, A., Itodo, H., (2010) Estimation of toxic metals in canned milk products from unlaquered tin plate cans, *Journal of American Science*, 6 (5), 173 - 178
7. Itodo, A., Itodo, H., (2010) Quantitative specification of potentially toxic metals in expired canned tomatoes found in village markets, *Nature and Science*, 8(4), 54 -58
8. Kocak, S., Tokusoglu, O., Aycan, S., (2005) Some heavy metal and trace essential element detection in canned vegetable foodstuffs by differential pulse polarography (DPP), *Electron. J. Environ. Agric. Food Chem.*, 4 (2), 871-878
9. Kowal, W., Beattie, O.B., Baadsgaard, H., & Krahn, P.M., (1991) Source identification of lead found in tissues of sailors from the Franklin Arctic Expedition of 1845. *Journal of Archeological Science*, 18, 193-203.
10. Ramonaityte, D.T. (2001) Copper, zinc, tin and lead in canned evaporated milk, Produced in Lithuania: the initial content and its change in storage. *Food Additives and Contaminants*, 18, 31-7.
11. Reilly, C. (2002) *Metal contamination of food: its significance for food quality and human health*, 3<sup>rd</sup> ed., Blackwell Science Ltd., 52-55
12. Rijk, R., Veraart, R., (2010) *Global legislation for food packaging materials*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim