Packaging Technology and Science
An International Journal

PACKAGING TECHNOLOGY AND SCIENCE
Packag. Technol. Sci. 2014; **27**: 787–797
DOI: 10.1002/pts.2069

Migration Processes of Metal Elements from Carbon Steel Cylinders to Food Gases

By Franco Tassi,[1,2]* Francesco Capecchiacci[2] and Orlando Vaselli[1,2]

[1]*Department of Earth Sciences, University of Florence, Via G. La Pira, 4, 50121, Florence, Italy*
[2]*CNR-IGG Institute of Geosciences and Earth Resources, Via G. La Pira 4, 50121, Florence, Italy*

This study is aimed to provide a protocol for sampling and analysis of metal elements migrating from carbon steel cylinders, used for gas storage and distribution, to food gases, i.e. those gases, such as CO_2, N_2 and O_2, employed by food and beverage industries. The concentrations of 23 selected elements, analysed by inductively coupled plasma mass spectrometry, in the three food gases collected from steel cylinders after a storage period of 50 days, were re-calculated considering (a) the initial concentrations (i.e. the concentrations of these elements in food gases before being packaged in carbon steel cylinders) and (b) a migration process of 5 years that proceeds in time following a linear trend.

Computed data were compared with the limit concentrations for mineral waters (CEE/CEEA/CE no. 83, 03-11-1998; D.Lgs no. 3, 2001; D.M. 29-12-2003), considering that the quantity of CO_2 commonly added to 1 L of mineral water is 5 g. Although no reference values indicating the concentration limits of metal contaminants in food gases are currently promulgated, the results of this comparison have evidenced that the highest concentrations of the most abundant elements among those selected for the test, i.e. Al, Cd, Cr, Cu, Fe, Mn, Ni and Pb, are up to 4 orders of magnitude lower that the previously cited limits. This suggests that the effects of migration of contaminants from carbon steel cylinders do not have a significant influence on the quality of food gases, independently on the type of food gas and carbon steel composition.

Received 22 April 2013; Revised 11 October 2013; Accepted 22 January 2014

KEY WORDS: migration process; food gases; packaging material; metal elements; carbon steel

INTRODUCTION

Recent European regulations (E.C. no. 1935/2004 and E.C. no. 2023/2006) impose controls of possible effects related to migration processes of contaminants from packages, including carbon steel cylinders, to *food gases*, which can be defined as those gases that are utilized by food and beverage industries for different applications, such as food preservation, ripening, spoilage prevention, freezing, chilling and carbonation. These regulations states that all materials and products in contact with food should be manufactured in compliance with the general and specific rules on guidelines for developing good manufacturing practices and standard operating procedures (http://www.haccpalliance.org/sub/food-safety/guifinal2.pdf). However, no laboratory tests have been provided to accomplish these requests in any stage of production, processing and distribution of food gases. A number of predictive mathematical models[1–10] and analytical strategies[11–14] were proposed to evaluate and quantify migrants from different types of polymeric packages to solid and liquid food, although much work is expected to be carried out for a correct estimation of the risk for human health related to the potential

---

* Correspondence to: Franco Tassi, Department of Earth Sciences, University of Florence, Via G. La Pira, 4, 50121 Florence, Italy.
E-mail: franco.tassi@unifi.it

exposure of the consumer to contaminating substances.[15–17] On the contrary, migration of metallic elements as a result of the contact of liquid and solid food with carbon steel has received scarce attention,[18,19] whereas, to the best of our knowledge, studies concerning migration processes between carbon steel packages and food gases are not available.

This study is aimed to (a) define a protocol for sampling and analysis of elements released in food gases (CO_2, N_2 and O_2) through migration processes from carbon steel cylinders and (b) use these analytical data to provide a preliminary evaluation of the impact of migration processes on food gas quality.

MATERIALS AND METHODS

Sampling and analytical protocol

The migration test was carried out for 36 carbon steel cylinders (12 cylinders for each food gas, i.e. CO_2, N_2 and O_2) of different inner volume (V: 5, 14 and 50 L) that were constructed by three different industries (IN1, IN2 and IN3), as listed in Table 1. Food gases were transferred from storage containers of five different production/distribution factories (FA1, FA2, FA3, FA4 and FA5; Table 1) to carbon steel cylinders by using tubing connectors commonly adopted for filling cylinders addressed to commercial use. Gas pressure (P) in N_2 and O_2 cylinders was ~200 bar, while that in CO_2 cylinders was ~50 bar. At each factory, an aliquot (40 L) of those gases sampled in cylinders was also collected in a plastic bag (a total of nine plastic bags; Table 1).

Once filled with gas, the cylinders were stored at ambient temperature for 50 days.

At the end of the storage period, the cylinder outlet valve was connected to a *liquid trap* through a transferring line constituted by a two-stage pressure regulator and a silicon tube (Figure 1). The liquid trap consisted of a 250-mL plastic dewar equipped with a gas bubble diffuser (Figure 1) and filled with 100 mL of a 1% HNO_3 solution in MilliQ water. The gas flux was set at 300 mL/min, in order to produce fine bubbles that interacted with the liquid phase where metal and metalloid elements of the gas phase were efficiently trapped. Gas flushing lasted for 10 h; thus, the total volume of gas flushed into the acidified solution from each cylinder was 180 000 cc. Gases stored in the nine plastic bags were flushed through the trapping solution immediately after sampling with the same equipment used for the gases extracted from the cylinders.

Once the transferring phase was completed, the acidified solution was stored into polyethylene bottles, ready to be analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Agilent 720ES) for P, S and Ti and inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7500CE) for Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Ni, Pb, Rb, Sb, Tl, Zn and Zr, without further treatments, according to the procedures described by the US Environmental Protection Agency (EPA): EPA 200.7 and EPA 6020A, respectively. ICP-AES and ICP-MS analyses were performed at the Gruppo

Table 1. General features (production industry, IN, distribution factory, FA, and food gas), volume (V, in litres) and pressure (P, in bars) of steel cylinders used for the test.

Factory	Gas	V	P	No. of cylinders	Industry	Bag
FA1	O_2	50	200	3	IN1	X
FA1	O_2	14	200	3	IN1	
FA1	CO_2	50	50	3	IN1	X
FA1	CO_2	14	50	3	IN1	
FA2	N_2	50	200	3	IN1	X
FA2	N_2	14	200	3	IN1	
FA3	CO_2	5	50	3	IN2	X
FA4	O_2	50	200	3	IN2	X
FA4	N_2	50	200	3	IN2	X
FA5	CO_2	50	50	3	IN3	X
FA5	O_2	50	200	3	IN3	X
FA5	N_2	50	200	3	IN3	X

Gas samples collected in bags are also reported.

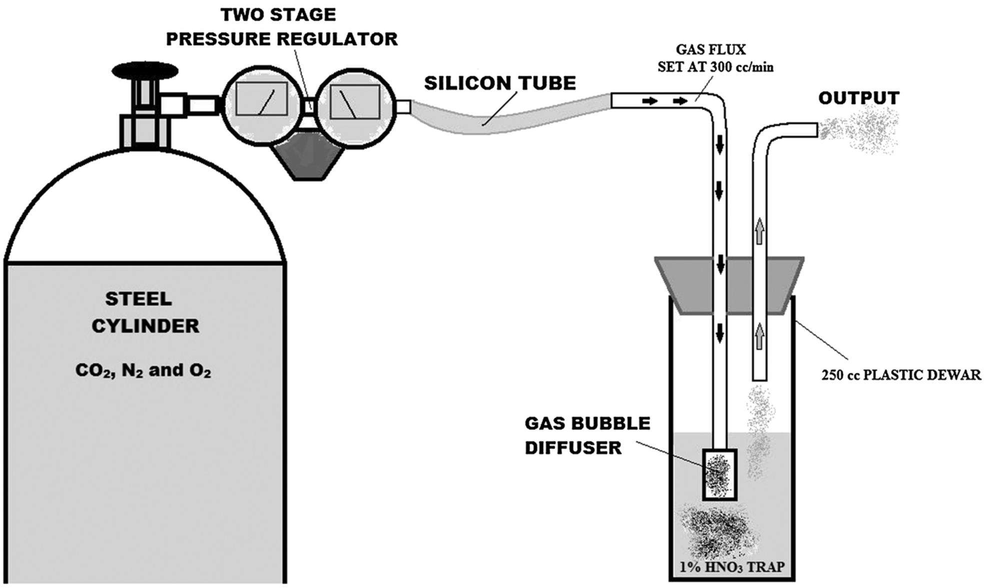

Figure 1. Schematic draft of the sampling apparatus used to collect metal and metalloid elements from food gases stored in steel cylinders.

CSA Ltd. Laboratories in Rimini (Italy), which is accredited by ACCREDIA, the latter being the Italian National Accreditation Body appointed by the state to perform accreditation activity, i.e. certifying the quality of both the methods used and the data obtained. The ICP analytical technique presents several

Table 2. Operating conditions for ICP-AES (wavelength) and the isotopes (ICP-MS) along with the number of replicates, relative standard deviation (RSD %), RF power, coolant gas flow, He flow, H_2 flow and detection limits.

ICP-AES	Wavelength (nm)	Replicates	RSD%	Detection limit (μg/l)
Phosphorous	214.914	3	5.3	10
Sulfur	182.03			20
Titanium	334.941	3	5.5	10
ICP-MS	Isotope	Replicates	RSD%	Detection limit (μg/l)
Aluminum (Al)	^{27}Al	3	11	0.1
Arsenic (As)	^{75}As			0.1
Boron (B)	^{11}B	3	5	0.1
Barium (Ba)	^{135}Ba	3	4.5	0.1
Cadmium (Cd)	^{114}Cd	3	4.5	0.1
Chromium (Cr)	^{52}Cr	3	13	0.1
Cobalt (Co)	^{59}Co	3	8.2	0.1
Copper (Cu)	^{63}Cu	3	6.2	0.1
Iron (Fe)	^{56}Fe	3	11	5
Mercury (Hg)	^{200}Hg	3	6	0.1
Lithium (Li)	^{7}Li	3	5	0.1
Manganese (Mn)	^{55}Mn	3	8.8	0.1
Nickel (Ni)	^{60}Ni	3	6.2	0.1
Lead (Pb)	^{208}Pb	3	11	0.1
Rubidium (Rb)	^{85}Rb	3	7	0.1
Antimony (Sb)	^{123}Sb	3	5	0.1
Thallium (Tl)	^{205}Tl			0.1
Zinc (Zn)	^{66}Zn	3	6.8	0.1
Zirconium (Zr)	^{90}Zr	3		0.1
	RF power (watt)	Coolant gas flow (l/min)	He flow (L/min)	H_2 flow (l/min)
ICP-AES	1200	15	3	3.4
ICP-MS	1550	15		

DOI: 10.1002/pts

Table 3. Concentrations of the 23 selected elements (in μg/L) in gases from the 36 cylinders and nine bags used for the test.

	O_2 bag	O_2	O_2	O_2	O_2	O_2	O_2	CO_2 bag	CO_2	CO_2	CO_2	CO_2
Factory	FA1	FA1	FA1	FA1	FA1	FA1	FA1	FA1	FA1	FA1	FA1	FA1
V		50.00	50.00	50.00	14.00	14.00	14.00		50.00	50.00	50.00	14.00
Al	2.20	2.76	2.12	1.96	2.79	2.65	2.65	2.70	3.34	3.50	3.71	3.30
As												
B												
Ba	0.09	0.07	0.06	0.05	0.13	0.10	0.11	0.12	0.16	0.15	0.11	0.14
Cd	0.03	0.05	0.04	0.05	0.02	0.02	0.02	0.04	0.09	0.04	0.04	0.01
Co		0.02	0.02		0.02				0.02	0.01		
Cr	0.06	0.14	0.13	0.08	0.14	0.11	0.06	0.06	0.07	0.08	0.08	0.04
Cu	1.02	0.31	0.37	0.40	1.04	0.88	0.98	0.55	0.48	0.43	0.48	0.33
Fe	2.80	2.97	3.54	2.95	3.02	3.54	2.96	4.10	6.38	5.70	5.95	5.38
Hg												
Li												
Mn	0.17	0.16	0.21	0.16	0.24	0.19	0.18	0.08	0.08	0.10	0.08	0.08
Ni	1.00	1.65	1.30	1.28	0.97	0.60	0.58	0.10	0.14	0.13	0.16	0.16
P												
Pb	0.02	0.04	0.02	0.02	0.03	0.02	0.02	0.02	0.04	0.03	0.02	0.02
Rb												
S												
Sb		0.03	0.01	0.01	0.02				0.01	0.01	0.01	
Se												
Ti												
Tl												
Zn	2.90	4.01	3.93	3.89	3.27	2.96	3.13	2.50	3.24	3.51	3.87	2.95
Zr												
	O_2 bag	O_2	O_2	O_2	N_2 bag	N_2	N_2	N_2	CO_2 bag	CO_2	CO_2	CO_2
Factory	FA4	FA4	FA4	FA4	FA4	FA4	FA4	FA4	FA5	FA5	FA5	FA5
V		50.00	50.00	50.00		50.00	50.00	50.00		50.00	50.00	50.00
Al	2.50	2.70	2.90	2.80	2.70	3.10	2.50	3.00	2.30	2.60	2.80	2.50
As												
B												
Ba	0.11	0.14	0.15	0.11	0.10	0.13	0.15	0.11	0.11	0.13	0.14	0.16
Cd	0.03	0.06	0.08	0.09	0.02	0.03	0.04	0.02	0.04	0.05	0.06	0.04
Co		0.01	0.01					0.01				
Cr	0.05	0.11	0.08	0.09	0.05	0.06	0.08	0.09	0.08	0.08	0.07	0.10
Cu	0.67	0.77	0.81	0.74	0.69	0.76	0.81	0.73	1.10	1.20	0.90	0.08
Fe	3.50	4.10	4.70	4.30	3.10	3.80	3.50	4.10	3.30	4.40	4.60	3.90
Hg												
Li												
Mn	0.37	0.39	0.43	0.44	0.36	0.45	0.39	0.41	0.19	0.21	0.18	0.22
Ni	0.90	1.20	1.30	1.00	0.80	1.30	1.20	1.50	1.20	1.60	1.50	1.80
P												
Pb	0.04	0.05	0.03	0.02	0.06	0.05	0.07	0.08	0.05	0.06	0.05	0.07
Rb		0.01	0.02				0.01	0.01				
S												
Sb												
Se												
Ti												
Tl												
Zn	3.10	3.30	3.50	3.20	2.90	3.40	3.20	3.30	2.50	3.50	3.40	3.60
Zr												

Element concentrations in the trapping solution (blank) are also reported. Acronyms are as in Table 1.

advantages with respect to other methods, such as atomic absorption spectrometry and inductively coupled plasma optical emission spectrometry that are commonly used for the analysis of metal and metalloid elements. ICP-AES and ICP-MS indeed have (a) a high sensitivity (up to 0.01 μg/L); (2) a

Table 3. Continued

CO_2	N_2 bag	N_2	N_2	N_2	N_2	N_2	N_2	CO_2	CO_2	CO_2
FA1 14.00	FA2	FA2 50.00	FA2 50.00	FA2 50.00	FA2 14.00	FA2 14.00	FA2 14.00	FA3 5.00	FA3 5.00	FA3 5.00
2.57	3.10	3.76	3.34	3.22	3.68	2.61	3.74	2.10	2.40	2.50
0.16	0.09	0.10	0.06	0.10	0.26	0.24	0.26	0.15	0.11	0.13
0.04	0.03	0.05	0.02	0.05	0.04	0.07	0.06	0.03	0.04	0.02
0.02							0.02			
0.06	0.07	0.11	0.11	0.08	0.08	0.08	0.08	0.12	0.11	0.09
0.38	0.71	1.06	1.06	1.02	0.99	0.95	0.93	0.46	0.51	0.53
5.32	3.90	4.91	4.54	5.09	4.07	4.71	4.05	3.40	2.90	3.10
					0.02	0.01	0.02			
0.10	0.11	0.10	0.12	0.14	0.10	0.10	0.12	0.23	0.26	0.21
0.15	1.90	2.34	2.20	2.40	2.24	1.89	1.61	1.10	1.20	1.50
0.03	0.03	0.06	0.04	0.06	0.07	0.05	0.05	0.04	0.06	0.04
		0.01			0.01		0.03			
0.01		0.01	0.01		0.01	0.01	0.01			
2.60	2.50	3.39	2.74	3.60	3.88	3.43	4.11	2.70	2.30	2.90
N_2 FA5 50.00	N_2 FA5 50.00	N_2 FA5 50.00	O_2 bag FA5	O_2 FA5 50.00	O_2 FA5 50.00	O_2 FA5 50.00	Blank			
2.60	2.70	2.40	2.10	2.20	2.50	2.40	0.15			
0.13	0.12	0.09	0.06	0.07	0.06	0.05				
0.08	0.06	0.04	0.03	0.05	0.05	0.04				
0.08	0.09	0.07	0.15	0.23	0.19	0.21	0.02			
0.62	0.60	0.52	0.24	0.33	0.26	0.28	0.02			
5.30	5.10	4.70	2.60	3.10	2.90	3.30	0.24			
0.11	0.13	0.10	0.15	0.19	0.21	0.18	0.01			
1.10	0.90	0.90	1.80	2.10	2.30	2.40	0.05			
0.07	0.06	0.04	0.06	0.08	0.08	0.07				
3.50	3.60	3.00	2.90	3.60	3.50	3.80	0.09			

relatively low analytical error (5%); and (c) an analysis run able to determine a high number of elements in the same aliquot.

The operating conditions for ICP-AES (wavelength) and the isotopes (ICP-MS) along with the number of replicates, relative standard deviation (RSD %) (determined when the analysed element was present),

DOI: 10.1002/pts

Table 4. Concentrations (in μg/L) of the 14 selected elements (in μg/L) detected in gases from the 36 cylinders corrected for the concentrations measured in the bags.

	O_2	O_2	O_2	O_2	O_2	O_2	CO_2	CO_2	CO_2	CO_2	CO_2	CO_2	N_2	N_2	N_2	N_2	N_2	N_2
Factory	FA1	FA1	FA1	FA1	FA1	FA1	FA1	FA1	FA1	FA1	FA1	FA1	FA2	FA2	FA2	FA2	FA2	FA2
V	50	50	50	14	14	14	50	50	50	14	14	14	50	50	50	14	14	14
Al	0.56			0.59	0.45	0.45	0.64	0.80	1.01	0.60	0.01		0.66	0.24	0.12	0.58		0.64
Ba				0.04	0.01	0.02	0.04	0.03		0.02	0.05	0.04	0.01		0.01	0.17	0.15	0.17
Cd	0.02	0.01	0.02				0.05						0.02		0.02	0.01	0.04	0.03
Co	0.02	0.02		0.02			0.02	0.01			0.03	0.02						0.02
Cr	0.08	0.07	0.02	0.08	0.05		0.01	0.02	0.02				0.04	0.04	0.01	0.01	0.01	0.01
Cu				0.02									0.35	0.35	0.31	0.28	0.24	0.22
Fe	0.17	0.74	0.15	0.22	0.74	0.16	2.28	1.60	1.85	1.28	0.45	1.22	1.01	0.64	1.19	0.17	0.81	0.15
Li																0.02	0.01	0.02
Mn		0.04		0.07	0.02	0.01		0.02				0.02		0.01	0.03			0.01
Ni	0.65	0.30	0.28				0.04	0.03	0.06	0.06	0.05	0.05	0.44	0.30	0.50	0.34		
Pb	0.02			0.01			0.02	0.01				0.01	0.03	0.01	0.03	0.04	0.02	0.02
Rb													0.01					0.03
Sb	0.03	0.01	0.01	0.02			0.01	0.01	0.01		0.01	0.01	0.01	0.01		0.01	0.01	0.01
Zn	1.11	1.03	0.99	0.37	0.06	0.23	0.74	1.01	1.37	0.45	0.30	0.10	0.89	0.24	1.10	1.38	0.93	1.61
	CO_2	CO_2	CO_2	O_2	O_2	O_2	N_2	N_2	N_2	CO_2	CO_2	CO_2	N_2	N_2	N_2	O_2	O_2	O_2
Factory	FA3	FA3	FA3	FA4	FA4	FA4	FA4	FA4	FA4	FA5	FA5	FA5	FA5	FA5	FA5	FA5	FA5	FA5
V	5	5	5	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
Al	0.20	0.50	0.60	0.20	0.40	0.30	0.40		0.30	0.30	0.50	0.20	0.50	0.60	0.30	0.10	0.40	0.30
Ba	0.02			0.03	0.04		0.03	0.05	0.01	0.02	0.03	0.05	0.02	0.01		0.01		
Cd		0.01		0.03	0.05	0.06	0.01	0.02		0.01	0.02		0.03	0.01		0.02	0.02	0.01
Co				0.01	0.01				0.01									
Cr	0.05	0.04	0.02	0.06	0.03	0.04	0.01	0.03	0.04			0.02	0.03	0.04	0.02	0.08	0.04	0.06
Cu				0.10	0.14	0.07	0.07	0.12	0.04	0.10			0.14	0.12	0.04	0.09	0.02	0.04
Fe	0.90	0.40	0.60	0.60	1.20	0.80	0.70	0.40	1.00	1.10	1.30	0.60	1.00	0.80	0.40	0.50	0.30	0.70
Li																		
Mn	0.05	0.08	0.03	0.02	0.06	0.07	0.09	0.03	0.05	0.02		0.03		0.01		0.04	0.06	0.03
Ni	0.40	0.50	0.80	0.30	0.40	0.10	0.50	0.40	0.70	0.40	0.30	0.60	0.30	0.10	0.10	0.30	0.50	0.60
Pb		0.01		0.01				0.01	0.02	0.01		0.02	0.02	0.01		0.02	0.02	0.01
Rb				0.01	0.02			0.01	0.01									
Sb																		
Zn				0.20	0.40	0.10	0.50	0.30	0.40	1.00	0.90	1.10	0.40	0.50		0.70	0.60	0.90

Acronyms are as in Table 1.

RF power, coolant gas flow, He flow, H_2 flow and detection limits are listed in Table 2. Appropriate internal standards, e.g. ^{6}Li, ^{45}Sc, ^{89}Y and ^{115}In, were used to set up the ICP-MS instruments.

RESULTS AND DISCUSSION

Analytical data (in μg/L) of 23 selected elements (Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Ni, P, Pb, Rb, S, Sb, Ti, Tl, Zn and Zr), determined in samples collected from the 36 cylinders and the nine plastic bags according to the procedure described in the previous section, are reported in Table 3. These data were computed by multiplying the analytical ICP-MS concentrations by the ratio between (a) the amount of gas flushed from the cylinders (353, 128 and 112 g for CO_2, O_2 and N_2, respectively) or the bags (80, 29 and 26 g for CO_2, O_2 and N_2, respectively) and (b) the weight of the trapping solution (100 g). From these values, the concentrations measured in the blank trapping solution were then subtracted.

The concentrations of nine elements were below the instrumental detection limits (As, B, S, Se, Ti, Tl and Zr: 0.1 μg/L; Hg: 0.05 μg/L, P: 0.01 μg/L), whereas Al, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn were detected in all the samples, their concentrations ranging from 0.02 to 6.38 μg/L. Eventually, Co, Li, Rb and Sb were only detected in few samples and their concentrations ranged from 0.01 to 0.03 μg/L.

In order to distinguish the contributions of food gas contaminants related to migration from carbon steel cylinders, which is the main goal of the present study, and those from other sources, the element concentrations measured in samples from the plastic bags were subtracted from those obtained from cylinders filled with the corresponding gas. The concentrations resulting from this computation (Table 4) are significantly lower with respect to those reported in Table 3, indicating that the measured metal and metalloid elements were mostly present in the filling gases before being stored in the cylinders. It is worth noting that some elements (Ba, Cd, Li, Rb and Sb) listed in Table 4 are not present in carbon steel even in trace amounts; thus, in principle, their presence in food gases should not be ascribed to migration processes. However, the concentrations of these elements were extremely low, suggesting that their occurrence is mostly dependent on the uncertainties of the analysis of samples from both the cylinders and the plastic bags. Iron, Zn, Ni and Al, showing concentrations up to 2 orders of magnitude higher than those of the other elements, seem to be the most prone to migrate from steel to food gases. As shown in Figure 2, the average concentrations of the contaminants in cylinders filled with O_2, CO_2 and N_2 are quite similar and do not show any specific trend, suggesting that the migration process does not significantly depend on the type of food gas. The comparable average concentrations measured in O_2 (Figure 3a) and, separately, N_2 (Figure 3b) and CO_2 (Figure 3c) from cylinders having a different volume (Table 1) demonstrate that migration is not dependent on the

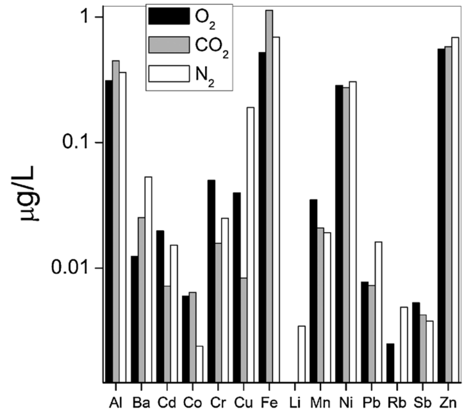

Figure 2. Column diagram of average concentrations (in μg/L) of Al, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Rb, Sb and Zn in samples from cylinders containing O_2 and, separately, CO_2 and N_2.

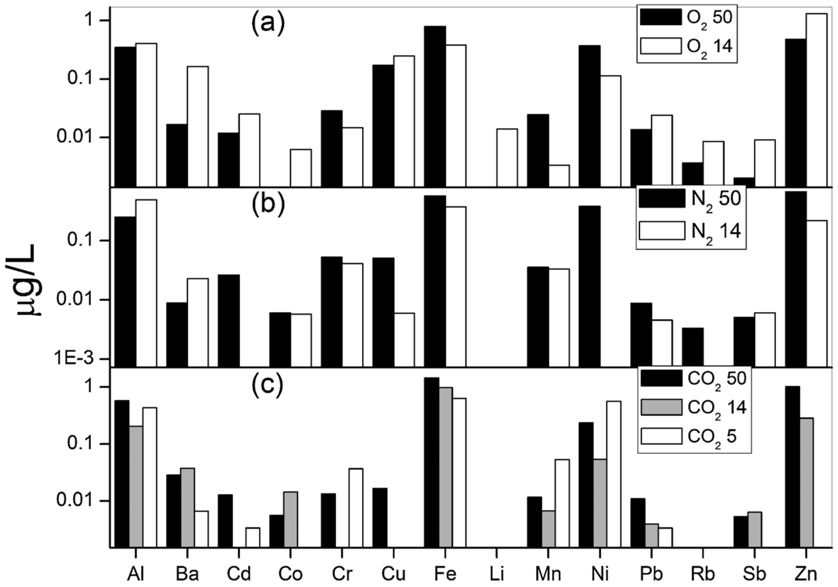

Figure 3. a–c. Column diagrams of average concentrations (in μg/L) of Al, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Rb, Sb and Zn in samples from cylinders with different volumes containing (a) O_2, (b) N_2 and (c) CO_2.

cylinder dimensions. Similarly, different types of carbon steel (IN1, IN2 and IN3) seem to produce comparable amounts of migrating contaminants (Figure 4a–c).

Although the European regulations (EC no. 1935/2004 and EC no. 2023/2006) do not indicate limit concentrations to assess the quality of food gases, which should be defined through appropriate laboratory and medical tests,[20–22] an evaluation of the effects of migration processes from carbon steel cylinders was tentatively carried out referring to the maximum admissible concentrations of Al, Cd, Cr, Cu, Fe, Mn, Ni and Pb in mineral waters in Italy (Table 5) reported by D.L. no. 31/2001 that received indication from the World Health Organization.[23,24] These limit concentrations (LC) were

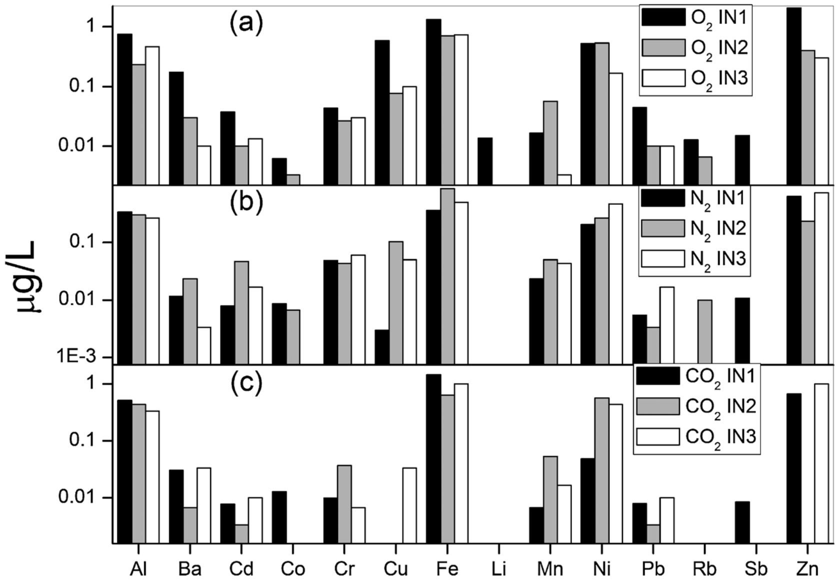

Figure 4. a–c. Column diagrams of average concentrations (in μg/L) of Al, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Rb, Sb and Zn in samples from cylinders contructed by different industries (IN1, IN2 and IN3) containing (a) O_2, (b) N_2 and (c) CO_2.

Table 5. Limit concentrations (LCs; in µg/L) of Al, Cd, Cr, Cu, Fe, Mn, Ni and Pb in mineral waters (D.L. no. 31/2001).

	LC
Al	200
Cd	3
Cr	50
Cu	1000
Fe	200
Mn	2000
Ni	20
Pb	100

compared with those measured in samples from CO_2-filled cylinders, considering that the maximum CO_2 concentrations in gasified mineral waters is 5 g/L. Analytical data of samples from N_2-filled and O_2-filled cylinders were not considered in these calculations because it is difficult to assess how and in which amount these gases, used for different applications by the food industry, are in contact with the consumer, making any comparison with the existing concentration limits, valid for various types of food, not reliable. To extend the validity of the test to the maximum shelf-life period of food gases in carbon steel cylinders (5 years), data of samples from CO_2-filled cylinders (Table 4) were multiplied by 36.5, i.e. the ratio between the days in 5 years (1825) and the days of test duration (50). Therefore, adopting this approach, the migration process was assumed to proceed in time following a linear trend, which is the worst case among those predicted by theoretical models based on the Fick's law.[25] As shown in Figure 5, re-calculated element concentrations are 2–4 orders of magnitude lower than the LCs, demonstrating that food gas contamination related to metallic element migration from carbon steel cylinders is not significant, even when the worst scenario is considered.

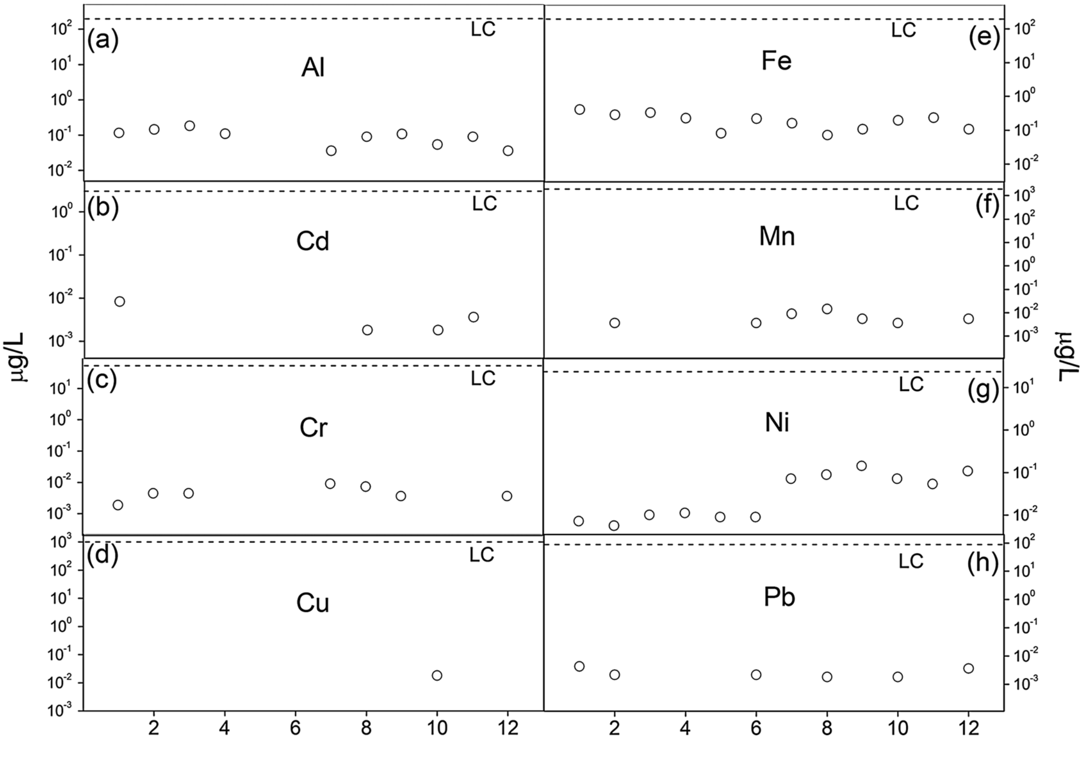

Figure 5. a–h. Concentrations (in µg/L) of (a) Al, (b), Cd, (c) Cr, (d) Cu, (e) Fe, (f) Mn, (g) Ni and (h) Pb in samples from CO_2-filled cylinders. To be compared with limit concentrations for mineral waters (LC), concentrations were recalculated considering (a) a storage period of 5 years and (b) a CO_2 concentration of 5 g/L.

DOI: 10.1002/pts

CONCLUSIONS

This study presents an efficient and simple sampling and analytical procedure, based on the use of an acidified trapping solution coupled with ICP-MS analysis, which is able to provide data that can be used for evaluating the impact on the food gas quality of migration of metallic elements from carbon steel cylinders. The definition of a methodological protocol is to be considered of fundamental importance because the European regulations impose a strict control on the quality of food in contact with packages of different material, including carbon steel, but they do not provide any guideline to indicate how to carry out these controls on food gases. Our tests showed that migration processes from carbon steel cylinders are able to transfer relatively low quantities of metallic elements (especially Al, Fe, Ni and Zn) in CO_2, N_2 and O_2, even if considering a long storage period (5 years). The amounts of these contaminants seem to be independent on the type of carbon steel and food gas. A preliminary evaluation of these results was carried out by comparing the element concentrations measured in CO_2-filled cylinders with the LCs for mineral waters. Although a correct estimation of the influence of migration processes on food gases should be based on reference values produced by specific toxicological studies on this particular type of packaging material and food, these tests have shown that CO_2 contamination related to migration from carbon steel cylinders is not significant.

ACKNOWLEDGEMENTS

The authors wish to thank Federchimica for their support for the development of the migration test. Careful and thoughtful comments and suggestions of two anonymous reviewers were warmly appreciated.

REFERENCES

1. Crank J. The mathematics of diffusion, 2nd edn. Clarendon Press: Oxford, 1975.
2. Pace RJ, Datyner AJ. Statistical mechanical model of diffusion of simple penetrants in polymers. I. Theory. *Journal of Polymer Science Polymer Physics Edition* 1979; **17**: 437–452.
3. Berens AR, Hopfenberg HB. Diffusion of organic vapors at low concentrations in glassy PVC, polystyrene and PMMA. *Journal of Membrane Science* 1982; **10**: 283–303.
4. Mercer A, Castle L, Comyn J, Gilbert J. Evaluation of a predictive mathematical model of di-(2-ethylhexyl) adipate plasticizer migration from PVC film into food. *Food Additives and Contaminants* 1990; **7**: 497–507.
5. Loubi S, Vergnaud JM. Process of contaminant transfer through a food package made of a recycled film and a functional barrier. *Packaging Technology and Science* 1995; **8**: 97–110.
6. Limm W, Hollifield HC. Modelling of additive diffusion in polyolefins. *Food Additives and Contaminants* 1996; **13**: 949–967.
7. Lau OW, Wong SK. Mathematical model for the migration of plasticizers from food contact materials into solid foods. *Analytica Chimica Acta* 1997; **347**: 249–256.
8. Brandsch J, Mercea P, Rüter M, Tosa V, Piringer O. Migration modelling as a tool for quality assurance of food packaging. *Food Additives and Contaminants* 2002; **19**: 29–41.
9. Helmroth IE, Rijk R, Dekker M, Jongen, W. Predictive modelling of migration from packaging materials into food products for regulatory purposes. *Trends in Food Science and Technology* 2002; **13**: 102–109.
10. Begley T, Castle L, Feigenbaum A, *et al*. Evaluation of migration models that might be used in support of regulations for food-contact plastics. *Food Additives and Contaminants* 2005; **22**(1): 73–90.
11. Begley T. Methods and approaches used by FDA to evaluate the safety of food packaging materials. *Food Additives and Contaminants* 1997; **14**: 6–7.
12. Castle L, MacArthur R, Mead EM, Read WA. Measurement uncertainty associated with overall migration testing. *Food Additives and Contaminants* 2004; **21**(3): 256–264.
13. Sendón García R, Sanches Silva A, Cooper I, Franz R, Paseiro LP. Revision of analytical strategies to evaluate different migrants from food packaging materials. *Trends in Food Science & Technology* 2006; **17**: 354–366.
14. Bueno-Ferrer C, Jimenez A, Garrigos MC. Migration analysis of epoxidized soybean oil and other plasticizers in commercial lids for food packaging by gas chromatography-mass spectrometry. *Food Additives and Contaminants* 2010; **27**(10): 1469–1477.
15. Vitrac O, Hayert M. Risk assessment of migration from packaging materials into foods. *AIChE Journal* 2005; **51**(4): 1080–1095.
16. Poças MF, Hogg T. Exposure assessment of chemical from packaging materials in foods: a review. *Trends in Food Science & Technology* 2007; **18**: 219–230.

DOI: 10.1002/pts

17. Jogsten IE, Perello G, Llebaria X *et al*. Exposure to perfluorinated compounds in Catalonia, Spain, through consumption of various raw and cooled foodstuffs, including packaged food. *Food and Chemical Toxicology* 2009; **47**: 1577–1583.
18. Stoewsand GS, Starner JR, Kosikowski FV, Morse RA, Bache CA, Lisk DJ. Chromium and nickel in acidic foods and by-products contacting stainless steel during processing. *Bulletin of Environmental Contamination and Toxicology* 1979; **21**, pp. 600-603.
19. Niklewicz M, Babuchiwski A, Dziuba B. Migration of metals from surfaces of steel equipment used in food industry. *Natural Sciences* 2000; **6**: 227–245.
20. Cullen AC, Frey HC. Probabilistic techniques in exposure assessment: A handbook for dealing with variability and uncertainty in models and inputs. Society of Risk Analysis: New York, 1999.
21. Arvanitoyannis IS, Bosnea L. Migration of substances from food packaging materials to foods. *Critical Reviews in Food Science and Nutrition* 2004; **44**: 63–76.
22. Holmes MJ, Hart A, Northing P, Oldring PKT, Castle L. Dietary exposure to chemical migrants from food contact materials: a probabilistic approach. *Food Additives and Contaminants* 2005; **22**(10): 907–919.
23. WHO. European standard for drinking water. World Health Organization: Geneva, 1998
24. WHO. Guidelines for drinking water quality. World Health Organization: Geneva, 2008.
25. Stoffers NH, Brandsch R, Bradley EL *et al*. Feasibility study for the development of certified reference materials for specific migration testing. Part 2: Estimation of diffusion parameters and comparison of experimental and predicted data. *Food Additives and Contaminants* 2005; **22**(2): 173–184.

DOI: 10.1002/pts