Contamination test of metal and non-metal elements from copper gas pipe to food gases

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In the last decade, EC regulations have been issued to minimize any interaction between packaging materials intended to come in contact with foodstuffs and potential contaminants. In this paper, the concentrations of 26 metals and metalloids in a food gas (CO2), possibly related to the migration of elements from copper pipes, which are commonly used during gas storage and distribution, were determined by ICP-AES and ICP-MS. A simple, though efficient, procedure to chemically trap these elements has shown that the copper pipes do not release significant concentrations of metals and metalloids, most of them being below or clustering below or around the instrumental detection limit. According to this study, only Al, Cu, Fe, Ni, and Zn can be related to the copper line. However, when considering the consumption of 3 L of water, at which 12 g/L of CO2 is added, the computed concentrations of metals and metalloids are 3 to 6 orders of magnitude lower than the limit concentrations in mineral waters intended for human consumption (European Directive 98/83/EC). This implies that the amount of contaminants in CO2 introduced in the human body is negligible.

KEYWORDS
analytical protocol, contamination process, food gases, metal elements, packaging material

1 INTRODUCTION

Regulation (EC) n° 1935/2004 requires that packaging of materials and articles intended to be in contact with foodstuffs is to be manufactured in compliance with Good Manufacturing Practices and Standard Operating Procedures (http://www.haccpalliance.org/sub/food-safety/guifinal2.pdf). Thus, under normal or foreseeable conditions of use, no transfer of contaminants, eg, metal elements, to food in quantities that could endanger human health, modify food composition or deteriorate organoleptic characteristics is expected. Food gases are those gases that are utilized by food and beverage industries for different applications, such as food preservation, ripening, spoilage prevention, freezing, chilling, and carbonation. Hence, management and use of packaging material used for food gases are dictated by the previously mentioned EC regulation.

A number of studies1-9 and analytical strategies10-13 were proposed to evaluate and quantify potential migrants from different types of polymeric packages to solid and liquid food. However, much work is still to be done for a correct estimation of the risk for human health related to the consumers’ exposure to contaminating substances.14,15 On the contrary, migration of metal elements due to the interaction of food with packaging materials has received scarce attention.16,17 A recent investigation18 has proposed an efficient sampling and analytical protocol to verify the possible impact of migration processes of trace elements from steel cylinders to food gases (ie, CO2, N2, and O2).

Based on that experience, in this work, experimental tests to evaluate the presence of contaminants in a food gas (CO2) related to the migration of elements from copper pipes that are commonly used during the activity of gas storage and distribution was carried out.

2 MATERIALS AND METHODS

2.1 Material and engineering of the test plant

The test was carried out on food-grade CO2 (E290) stored in a ~45-m-long copper pipe (diameter 12 mm, thickness 1 mm) with 17 curves having a curvature radius ≥ 5 times the internal diameter of the pipe and 4 braze welding. The copper pipe was equipped with a safety valve (maximum pressure 16 bar) for plant protection. The whole system used for the test consisted of 3 blocks (Figure 1): (1) a pre-heating and gas decompression unit for gas injection to the copper pipe; (2) the copper pipe; and (3) ON/OFF valves and pressure regulation (second and third stage) valves, to carry out the gas sampling. The ON/OFF
and pressure regulation (second and third stage) valves were consisting of: (1) a low-pressure shut-off valve (Model 50-0.12 DVA); (2) a DC 50 low-pressure reducer (second stage); (3) a shut-off valve (Model 50-0.12 DVA); and (4) a DC 50 low-pressure reducer (third stage).

The 50-0.12 DVA valve, as well as the DC 50 reducers, was made of Ni-plated brass, with shutter and membrane in PTFE-Hastelloy® and NBR, respectively. The unit used to transfer CO₂ from the steel cylinder (CO₂ source) to the copper pipe consisted of (1) flexible steel cylinder connection with steel connector and brass nut; (2) an electric heater 500 W [Rechauffeur] and a ECOGAZ SA200-15/11-80 decompression unit made of steel and brass parts. It also included gaskets and connections in polyamide, aluminum, and PTFE-EPDM. All the used materials are compatible with the CO₂ involved in the test, according to 97/23/CE directive 29/05/97 class IV^ module H1.

2.2 | Sampling and analytical procedure

The gas used for the test was transferred from the steel cylinder (CO₂ source) to the copper pipe after being heated to obtain an initial operative pressure of 15 bar. Once filled (time 0; on April 4, 2016), the pipe was left at ambient conditions. The gas sampling from the copper pipe was carried out at a reduced flux (10 L/min) up to the complete filling of the Tedlar bag.

Five gas samples (10 L) were collected in Tedlar plastic bags (Figure 2) (Table 1), after 1 day and 1, 2, 4, and 6 weeks. One gas sample was also collected from the steel cylinder (CO₂ source) as “blank” reference data.

At the Laboratory of Fluid Geochemistry (Department of Earth Sciences—University of Florence, Italy), the gases stored in the Tedlar bags were gently flushed through an acidified solution by connecting, through a silicon tube, the screw-cap valve of the bags to the liquid
TABLE 1  Concentrations (in mg/kg) of the 26 selected elements in CO₂ from the copper pipe; b.d.l. = below detection limit. Detection limit corresponds to the first point of the calibration line

<table>
<thead>
<tr>
<th>mg/kg CO₂</th>
<th>Cylinder</th>
<th>1 day</th>
<th>1 week</th>
<th>2 weeks</th>
<th>4 weeks</th>
<th>6 weeks</th>
<th>Detection limits</th>
<th>Instrumental linear range, μg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>2.5E−03</td>
<td>1.0E−03</td>
<td>5.0E−04</td>
<td>2.0E−03</td>
<td>5.0E−04</td>
<td>5.0E−04</td>
<td>3.0E−04</td>
<td>0.1−50</td>
</tr>
<tr>
<td>Al</td>
<td>3.0E−03</td>
<td>2.0E−03</td>
<td>5.0E−03</td>
<td>3.5E−03</td>
<td>4.5E−03</td>
<td>1.0E−03</td>
<td>2.5E−04</td>
<td>0.5−250</td>
</tr>
<tr>
<td>As</td>
<td>3.5E−05</td>
<td>3.5E−05</td>
<td>b.d.l.</td>
<td>3.5E−05</td>
<td>3.5E−05</td>
<td>2.5E−05</td>
<td>b.d.l.</td>
<td>0.1−250</td>
</tr>
<tr>
<td>Ba</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>5.0E−04</td>
<td>0.1−20</td>
</tr>
<tr>
<td>Cd</td>
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<td>4.5E−04</td>
<td>2.5E−04</td>
<td>5.5E−04</td>
<td>2.5E−04</td>
<td>2.5E−04</td>
<td>2.0E−04</td>
<td>0.1−250</td>
</tr>
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<td>Cs</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>5.0E−04</td>
<td>0.1−20</td>
</tr>
<tr>
<td>Co</td>
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<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>5.0E−05</td>
<td>0.1−250</td>
</tr>
<tr>
<td>Cr</td>
<td>1.0E−04</td>
<td>5.0E−05</td>
<td>5.0E−05</td>
<td>1.0E−04</td>
<td>5.0E−05</td>
<td>5.0E−05</td>
<td>5.0E−05</td>
<td>0.1−250</td>
</tr>
<tr>
<td>Cu</td>
<td>3.0E−04</td>
<td>2.5E−04</td>
<td>2.0E−03</td>
<td>1.0E−03</td>
<td>4.0E−04</td>
<td>5.0E−04</td>
<td>1.0E−04</td>
<td>0.1−250</td>
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<tr>
<td>Fe</td>
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<td>b.d.l.</td>
<td>b.d.l.</td>
<td>4.5E−03</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>2.5E−03</td>
<td>5−400</td>
</tr>
<tr>
<td>Hg</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>5.0E−05</td>
<td>0.1−50</td>
</tr>
<tr>
<td>Li</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>5.0E−05</td>
<td>0.1−250</td>
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<tr>
<td>Mn</td>
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<td>1.0E−04</td>
<td>6.5E−05</td>
<td>1.7E−04</td>
<td>3.5E−05</td>
<td>3.5E−05</td>
<td>3.0E−05</td>
<td>0.1−250</td>
</tr>
<tr>
<td>Ni</td>
<td>1.5E−04</td>
<td>2.5E−04</td>
<td>2.0E−03</td>
<td>1.0E−03</td>
<td>4.0E−04</td>
<td>5.0E−04</td>
<td>1.0E−04</td>
<td>0.1−250</td>
</tr>
<tr>
<td>P</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>5.0E−02</td>
<td>0.01−10</td>
</tr>
<tr>
<td>Pb</td>
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<td>5.0E−05</td>
<td>2.0E−04</td>
<td>1.5E−04</td>
<td>1.0E−04</td>
<td>1.0E−04</td>
<td>5.0E−05</td>
<td>0.1−250</td>
</tr>
<tr>
<td>Rb</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>5.0E−05</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>5.0E−05</td>
<td>0.1−20</td>
</tr>
<tr>
<td>S</td>
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<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>5.0E−02</td>
<td>0.01−20</td>
</tr>
<tr>
<td>Sb</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>5.0E−05</td>
<td>0.1−250</td>
</tr>
<tr>
<td>Se</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>2.5E−04</td>
<td>0.5−250</td>
</tr>
<tr>
<td>Si</td>
<td>2.0E−01</td>
<td>1.0E−01</td>
<td>5.0E−02</td>
<td>1.0E−01</td>
<td>2.0E−01</td>
<td>1.0E−01</td>
<td>1.0E−02</td>
<td>5−400</td>
</tr>
<tr>
<td>Sn</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>5.0E−05</td>
<td>0.5−250</td>
</tr>
<tr>
<td>Ti</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>5.0E−05</td>
<td>0.1−250</td>
</tr>
<tr>
<td>Tl</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
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<td>0.1−250</td>
</tr>
<tr>
<td>Zn</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>2.0E−03</td>
<td>4.5E−03</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>2.0E−03</td>
<td>5−400</td>
</tr>
<tr>
<td>Zr</td>
<td>3.5E−04</td>
<td>2.0E−04</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>3.0E−04</td>
<td>0.1−250</td>
</tr>
</tbody>
</table>

trap. The latter was consisting of a 70-mL glass bubbler (Figure 3), preventively cleaned in a suprapur HCl bath and abundantly rinsed with MilliQ, filled with 30 mL of 1% HNO₃-acidified MilliQ water. The gas flux was set at 250 cc/min, in order to efficiently trap into the liquid phase metal and metalloid elements possibly present in the gas phase. Once the gas-transfer phase was completed, the acidified solution was stored into polyethylene bottles, to be analyzed 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 7500 CE) for Ag, Al, As, B, Ba, Cd, Ce, Co, Cr, Cu, Fe, Hg, Li, Mn, Ni, Pb, Rb, S, Sb, Se, Si, Sn, Ta, Ti, Zn, and Zr, without further treatments, according to the procedures described by the US Environmental Protection Agency (EPA 200.7 and EPA 6020A, respectively). Each sample was analyzed being collected from the pipe and transferred to the liquid trap. The ICP-AES and ICP-MS analyses were carried out at the Gruppo 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, ie, certifying the quality of both the methods used and the data obtained. The selected analytical techniques provided several advantages with respect to other methods, such as atomic absorption spectrometry, which is commonly used for the determination of metal

FIGURE 3  Glass bubbler with trap solution
and metalloid elements. ICP-AES and ICP-MS indeed have (1) a low detection limit (down to 0.01 µg/L), (2) a relatively low analytical error (5%), and (3) the capability to determine a high number of elements in the same analytical run. In both techniques, 3 replicates were carried out for each analysis. Consequently, the final result is referred to the mean value of 3 repetitions.

Internal standards to set up the ICP-AES and ICP-MS were Bi, Ho, In, ²⁴Li, Sc, Tb, and Y and ⁴⁰Ca, ⁵⁷Co, ⁷⁰Zr, and ¹ⁱ⁵In, respectively. Standard solutions were prepared by opportune dilution of each single element starting from 1000 mg/L solutions.

3 | RESULTS AND DISCUSSION

Analytical data (expressed in mg/kg) of 26 selected elements (Ag, Al, As, Ba, Cd, Ce, Co, Cr, Cu, Fe, Hg, Li, Mn, Ni, P, Pb, Rb, S, Se, Si, Sn, Ta, Ti, Zn, and Zr), determined in the samples from food CO₂ cylinder and the copper pipe and collected according to the procedure and the time schedule described in the previous section, are reported in Table 1.

The analytical data were computed through several steps, as follows: (1) the analytical concentrations (in mg/L of water) measured in the trap solution (blank) were subtracted to those measured in the samples from the copper pipe, ie, those where 20 g of CO₂ (corresponding to 10 L of gaseous CO₂) were collected; (2) the amounts of contaminants measured in 20 g of CO₂ (in mg) were then calculated, according to the following equation:

\[
X_{mg} = \frac{X_{mg/L of water} \times V}{1000}
\]

where X is the analyte and V is the volume of the liquid in the bubbler after the sampling (expressed in mL); (3) the data were then expressed in mg/kg (kg of CO₂), according to the following equation:

\[
X_{mg/kg} = \frac{X_{mg} \times 1000}{20}.
\]

As shown in Table 1, the concentrations of 12 elements were below the instrumental detection limits (b.d.l.), whereas Ag, Al, Cd, Cr, Cu, Mn, and Pb were detected in all the samples, their concentrations ranging from 0.000035 to 0.005 mg/kg. The concentrations of Si ranged from 0.05 to 0.2 mg/kg. Eventually, As, Fe, Ni, Rb, Zn, and Zr were detected in some samples and their concentrations were between 0.000035 and 0.0045 mg/L.

The amounts of contaminants possibly released from the copper pipe were calculated by subtracting the measured values in CO₂ from the steel cylinder (before the gas storage within the copper pipe; first column in Table 1) to those measured in CO₂ from the copper pipe after the different storage periods. As shown in Table 2, where the concentration data of the gas stored in the copper pipe were computed by subtracting those measured in the gas from the cylinder (blank), most elements potentially related to contamination from the copper pipe are absent or present (Al, Cd, Cu, Fe, Mn, Ni, Rb, and Zn) at very low concentrations (<0.0045 mg/kg). It is worth noting that Cd and Rb, which were measured in some of the analyzed gases, are not present in industrial copper even in trace amounts. Thus, they can unlikely be ascribed to the copper line. On the other hand, Al, Cu, Fe, Mn, Ni, and Zn, which are found in trace amounts in industrial copper, showed concentrations, not in agreement with any temporal trend consistent with a migration process from copper (Figure 4). In fact, the progressive release of contaminants from a package, including copper, is expected to produce increasing (cumulative) contaminant concentrations in time.¹⁹ Because the temporal variation showed alternating spike concentrations and values clustering around or below the instrumental detection limit, it is reasonable to suggest that these elements are not related to the copper pipes. Thus, the sporadic presence of small-size solid particles in the sourced gas may likely explain the origin of these elements. This is also supported by the fact that copper is less abundant than other contaminants (eg, Al, Zn, and Fe; Tables 1 and 2), implying that element migration from the copper pipes is not consistent with the measured data.

Although the European regulations (EC no. 1935/2004 and EC no. 2023/2006) do not indicate threshold concentrations to assess the quality of food gases, which should be defined through appropriate laboratory and medical tests,²⁰,²¹ it is not possible to directly provide an estimation of the effective contamination of CO₂ independently on the process(es) responsible for the occurrence of the detected contaminants. A tentative assessment was carried out by comparing the
measured values to the Specific Release Limits (SRLs) for metals and alloy components (expressed in mg/kg of food) (edqm). It is worth noting that the measured values are 1 to 5 orders of magnitude lower than those of SRL (Table 3).

Because it is not reliable to consider CO2 as pure food, a more realistic evaluation of the level of contamination in the CO2 was obtained by comparing the maximum measured concentrations (worst scenario) of the contaminants (specifically Al, Cd, Cu, Fe, Mn, Ni and Zn) to their limit concentrations (LCs) in mineral waters for human consumption (European Directive 98/83/EC). If the addition of 12 g of CO2 to 1 L of water and a daily average consumption of 3 L of waters per person are considered, a total of approximately 36 g of CO2 is ingested per day. According to these considerations, the computed concentrations are 3 to 6 orders of magnitude lower than the LCs (Table 4). Hence, the amount of contaminants in CO2, independently on their origin, has to be regarded as negligible even when the highest concentrations recorded in the present study are taken into account.

### 4 | CONCLUSIONS

This study reports the results of an efficient and simple sampling and analytical procedure for evaluating the impact on the food gas (CO2) quality of contaminant transferred from copper material. Our measurements, carried out on CO2 samples collected from a copper line specifically constructed to carry out this study, excluded that migration processes, ie, the progressive release of chemical elements from copper, are not able to produce a significant contamination of the food gas. Only small amounts of metal elements, possibly related to the copper line (Al, Cu, Fe, Ni, and Zn), and the sourced gas (Cd, Mn, and Rb) were detected. These findings indicate that the presence of these contaminants in CO2 was likely due to the sporadic occurrence of fine solid particulate in the source gas, ie, present in CO2 before it was transferred into the copper pipe. Although a correct estimation of the CO2 quality should be based on reference values produced by specific toxicological studies on this particular type of packaging material.
and food, a comparison with SRL and LC values clearly showed that CO₂ had a satisfactory degree of purity. To obtain further insights on the source of the contaminants, tests at dynamic conditions (i.e. sampling of CO₂ continuously flushing in a copper tube) are to be carried out as possible future development.

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