

Emissions of polycyclic aromatic hydrocarbons and polycyclic carbonyl biphenils from electric arc furnaces^(·)

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Abstract

This paper describes work done in order to determine the emissions of highly toxic organic micropollutants from electric arc furnaces used in the production of carbon steel from scrap. The study will be allowing to derive relationships between the levels of airborne micropollutants and the operational parameters of the production process so that an abatement of pollution could be achieved. By using the European standard method CEN 1948 for dioxin like compounds sampling and measurement, it was possible to determine the characteristic fingerprint of micropollutants such as polycyclic aromatic hydrocarbons (PAHs) and polycyclic carbonyl biphenils (PCBs) emitted by this particular stationary source.

Keywords

PAHs. PCBs. Iron and steel industry. Electric arc furnace.

Emisiones de hidrocarburos aromáticos policíclicos y bifenilos carboxilados policíclicos en hornos eléctricos de arco

Resumen

Este artículo contiene resultados del trabajo ejecutado para estudiar la determinación de las emisiones de los micropolutantes orgánicos muy tóxicos que se emiten por los hornos eléctricos de arco utilizados en la producción de acero. Este estudio inicial va a permitir relacionar las concentraciones de polutantes emitidos a la atmósfera con las condiciones de operación del horno eléctrico de arco. Utilizando el método normalizado CEN 1948 para captación y análisis de muestras de compuestos análogos a las dioxinas ha sido posible determinar el perfil característico de los micropolutantes tales como PAHs y PCBs emitidos por esta fuente.

Palabras clave

PAHs. PCBs. Industria del acero. Horno eléctrico de arco.

1. INTRODUCTION

In a previous paper^[1], the author described a study on the evaluation and assessment of dioxin (PCDDs) and dibenzofurans (PCDFs) atmospheric emissions from electric arc furnace (EAF) steel making process. In particular, when ferrous scrap results from the automobile industry it frequently includes plastics such as polyvinylchloride, thus resulting in atmospheric emissions of dioxin like compounds. Apart from plastics other organic compounds that could act as PCDDs and PCDFs precursors can be found in scrap used as raw material for steel production by this process.

It is well known^[2] that PCBs, unlike other highly toxic compounds such as PCDDs and PCDFs have been produced industrially, bearing in mind their specific physico-chemical properties that could be used in several applications. In fact, they are almost non-combustible, have very low vapour pressures at room temperature, are non-volatile and non-soluble, have considerable thermal and chemical stability, resistant both to acid and alkali substances. Therefore, they have been used as dielectric fluids used in electrical transformers and condensers; as adhesives, paints, hydraulic lubricants, etc. Nevertheless, its toxicity has been widely demonstrated, which resulted in the restriction of PCBs for use in several applications. Both PCBs and PAHs have been

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reported as emitted from the steel and metallurgic industries, namely when scrap is melted again in recycling processes, such as steel making from scrap via the EAF process^[3 and 4].

2. EXPERIMENTAL

In order to attain the project objectives, a set of sampling campaigns, followed by laboratorial analysis, have been undertaken at the stacks of the dedusting units of a Portuguese EAF located in Northern Portugal. The specific characteristics of the plant, as well as of the installed equipment were described previously by the author^[1].

The sampling technique was based on the European Standard method EN1948^[5-7], which specifically concerns dioxin and dibenzofuran sampling and analysis. However, certain modifications were introduced in order to isokinetically sample PAHs and PCBs. The analytical determinations were performed in a HRGC/HRMS, VG-AutoSpec using capillary columns DB5. PAHs analysis included the determinations of 16 congeners, defined according USEPA, using deuterated extracts ranging from D⁸ to D¹⁴, as follows:

Naphthalene,	Benzo(a)anthracene,
Acenaftalene,	Crisene,
Acenaftene,	Benzo(b)fluorantene,
Fluorene,	Benzo(k)fluorantene,
Fenantrene,	Benzo(a)pirene,
Anthracene,	Indene(1,2,3)-cd-pirene,
Fluorantene,	Benzo(ghi)perilene,
Pirene,	Dibenzo(ah)anthracene

Regarding PCBs, the analysis covered the isomers 28, 52, 101, 138, 153, 180 and total homologue, using internal standards marked with ¹³C. For the utilized sampling volumes, the detection limit both for PAHs and PCBs was determined at 0.01 mg/m³. The basic sampling procedure, using a cooled probe, was described previously^[1]. The sampling time was now considerably reduced, from the sampling time necessary for PCDDs/PCDFs, to about an hour. Particulate matter was collected on a filter and the gaseous phase was collected by condensation on an adsorbent agent. After sample recovery, the sampling train was decontaminated using water and acetone. Filters and adsorbents are mixed together for extraction with an organic solvent by soxhlet and then concentrated in a rotovapour device. It is necessary to remove any interferents from the final extract before performing the chromatographic analysis by HRGC/HRMS. The determinations are

made by adding internal and external deuterated standards as follows:

Naphthalene	D ₈
Acenaftalene	D ₁₀
Fenantrene	D ₁₀
Pirene	D ₁₀
Benzo(k)fluorantene	D ₁₂
Benzo(a)pirene	D ₁₂
Dibenzo(ah)anthracene	D ₁₄
Benzo(ghi)perilene	D ₁₂

The same sample was used for determination of PCB 28, 52, 101, 138, 153, 180 and total homologue. This later determination was made using the following internal standards:

2,4,4'-Tri-PCB (PCB-28)	¹³ C-UL
2,2',5,5'-Tetra-PCB (PCB-52)	¹³ C-UL
2,2',4,5,5'-Penta-PCB (PCB-101)	¹³ C-UL
2,2',3,4,4',5'-Hexa-PCB (PCB-138)	¹³ C-UL
2,2',4,4',5,5'-Hexa-PCB (PCB-153)	¹³ C-UL
2,2',3,4,4',5,5'-Hepta-PCB (PCB-180)	¹³ C-UL

After the addition of standards, samples were extracted with nanograde specific solvents. The procedure for interferent removal, already described for PAHs, was also used here prior to the chromatographic determination

3. RESULTS AND DISCUSSION

Within the scope of European standards there is no standardized method for the determination of the uncertainty of measurement that covers both sampling and the analytical procedure as well as the uncertainty related with the conditions of the sampling site in special. For this reason the single results are not supplied with information of uncertainty. Our experience shows that, in general, uncertainties in the range of 10 % to 20 % for the components listed in the above tables. For values near the detection limit the uncertainties are higher. Based on the measurements made, figure 1 shows the existence of individual species of PAHs, where a prominence of naphthalene, acenaftalene, fenantrene and fluorene could be noticed. Other species such as fluorantene, pirene, acenaftene and crisene were also found in lower amounts. As a whole, the existence of 12 of the 16 searched species of PAHs was verified, as benzo(a)pirene, indene(1,2,3)-cd-pirene, benzo(ghi)perilene and dibenzo(a,h)anthracene were not detected.

Carefully observing this figure, with a zoom from anthracene on, the existence of a coherent profile is

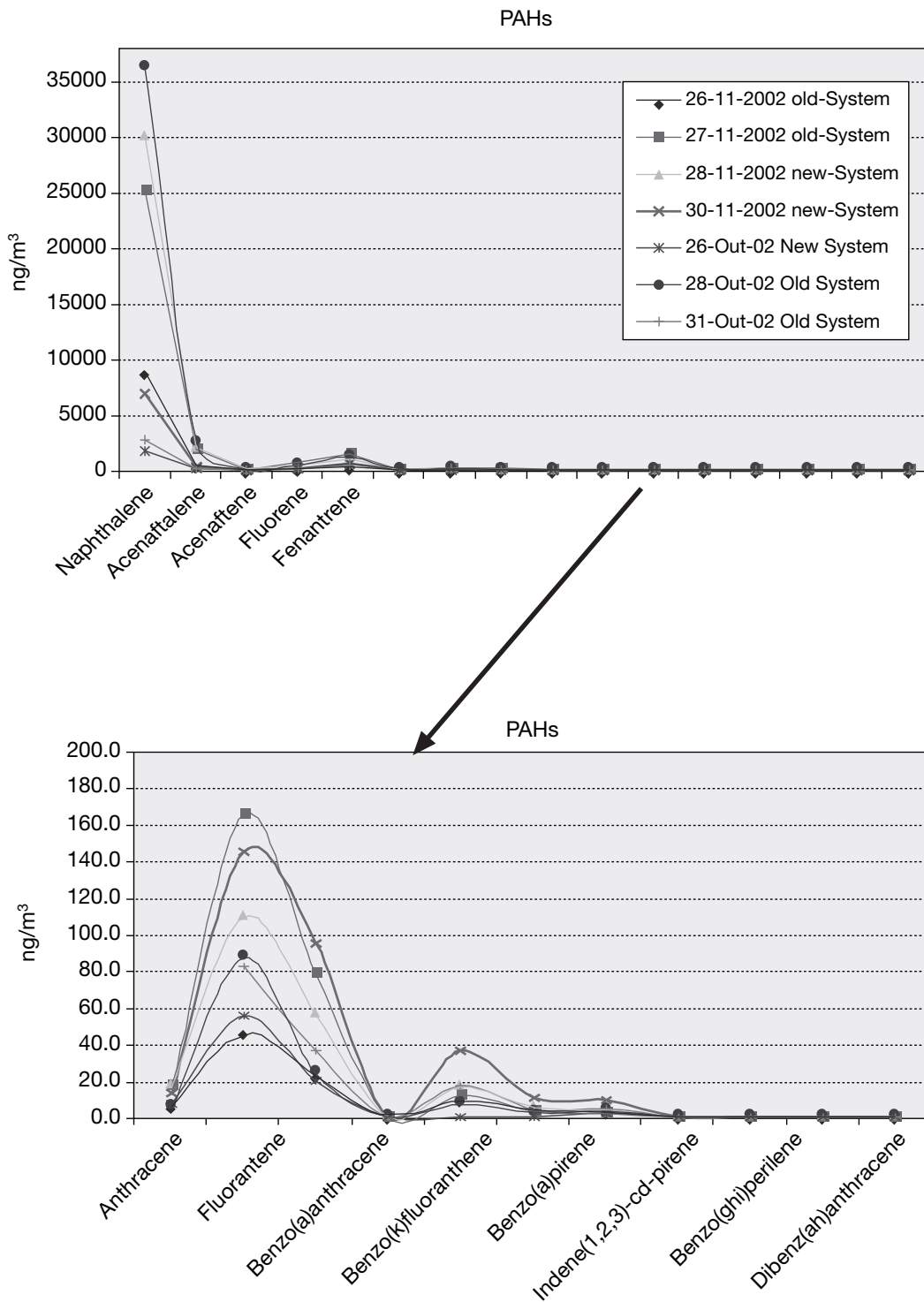


Figure 1. Profile of PAHs obtained in 7 measurements.

Figura 1. Perfil de concentraciones de PAH obtenido en 7 medidas.

also verified, and this is the actual “fingerprint” of this process in terms of PAHs emissions. In fact, it can be noted that this profile is always observed during the operation of this EAF system and is non-dependant of the gas flow rate neither of the

EAF actual processing capacity. The observed variations can possibly be explained by different production regimes, using different loads for the furnace, which were observed during sampling operations. Table I presents the main physical and

Table I. Physico-chemical properties of PAHs [2]

Tabla I. Propiedades físico-químicas de los PAH [2]

PAHs	Nº of rings	Mol. Weight (g/mol)	Fusion point (°C)	Boiling point (°C)	Chemical Formula
Naphthalene	2	128	80.6	218	C ₁₀ H ₈
Acenaftalene	3	152	94	265	C ₁₂ H ₈
Fenantrene	3	178	99.5	340	C ₁₄ H ₁₀
Fluorene	3	166	116	295	C ₁₃ H ₁₀
Acenaftene	3	154	95	279	C ₁₂ H ₁₀
Anthracene	3	178	217	370	C ₁₄ H ₁₀
Fluorantene	4	202	110.8	375	C ₁₆ H ₁₀
Pirene	4	202	156	404	C ₁₆ H ₁₀
Crisene	4	228	255	448	C ₁₈ H ₁₂
Benzo(a)anthracene	4	228	159.8	437.6	C ₁₈ H ₁₂
Benzo(a)pirene	5	252	176	495	C ₂₀ H ₁₂
Dibenzo(a,h)anthracene	5	278	266	524	C ₂₂ H ₁₄
Benzo[k]fluorantene	5	252	215.7	480	C ₂₀ H ₁₂
Benzo[b]fluorantene	5	252	167	357	C ₂₀ H ₁₂
Indeno(1,2,3)-cd-pirene	6	276	162.5	536	C ₂₂ H ₁₂
Benzo(g,h,i)perilene	6	276	278	500	C ₂₂ H ₁₂

chemical properties [2] of the measured PAHs. It can be noticed that the species that were not found present in the stack emissions are the species with 5 and 6 benzenic rings, which have strongly adhered to dust particles and, thus are collected by bag filters, as dust capturing devices.

The results of PCBs show a decrease of concentration with the increase of chloride atoms present in the PCB compound, as shown in figure 2. The higher content compounds are the ones having lower number of chloride atoms.

Table II presents the main physico-chemical properties of the analysed PCBs [2]. The observed trend seems to be coherent with those properties: both the fusion and the boiling points increase with the number of chlorine atoms, as well as with molecular weight. On the contrary, the vapour pressure and the evaporation rate at 25 °C decrease with the number of chlorine atoms, and this result in a decrease of concentrations observed in the emissions.

4. CONCLUSIONS

These studies have, so far, allowed to derive some important conclusions on the emission of gaseous micropollutants, making possible to determine the

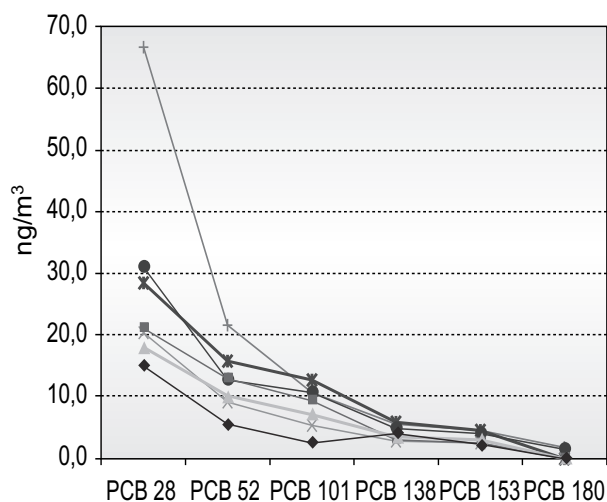


Figure 2. Profile of PCBs obtained in 7 measurements.

Figura 2. Perfil de concentraciones de PCB obtenido en medidas.

characteristic profile (also known as “fingerprint”) of PCDDs/PCDFs as well as PAHs and PCBs.

In fact, in spite of some observed variability in successive sampling campaigns, it was possible to determine regular concentration profiles of the gaseous emissions of PAHs and PCBs. This is the

Table II. Physico-chemical properties of PCBs [2]*Tabla II. Propiedades físico-químicas de los PCB [2]*

PCBs	Nº of chlorine Atoms	Mol. Weight (g/mol)	Boiling point (°C)	Fusion point (°C)	Vapour pressure at 25 °C (Pa)	Evaporation rate at 25°C (g/(m ² h))
PCB 28	3	256	28-87	337	0.054	0.017
PCB 52	4	290	47-180	360	0.012	4.2 x10 ⁻³
PCB 101	5	324	76.5-124	381	2.6x10 ⁻³	1.0x10 ⁻³
PCB 138	6	358	77-150	400	5.8x10 ⁻⁴	2.5x10 ⁻⁴
PCB 153	6	358	77-150	400	5.8x10 ⁻⁴	2.5x10 ⁻⁴
PCB 180	7	391	122.4-149	417	1.3x10 ⁻⁴	6.2x10 ⁻⁵

basic information that will allow, further on, to derive further conclusions on the mechanisms of formation/destruction of these species and, at a further stage, to define operational strategies to perform the abatement of these emissions.

It should be noted that the observed existence of PAH and PCB species, which are PCDDs/PCDFs precursors, could easily result in the formation of PCDDs/PCDFs congeners by the means of heterogeneous reactions, on the surface of particles and dust that occur at temperatures higher than 300 °C [8].

Acknowledgments

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