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The Two Smells of Touched or Pickled Iron – (Skin) Carbonyl-Hydrocarbons and Organophosphines

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List of used chemical species and their CAS numbers

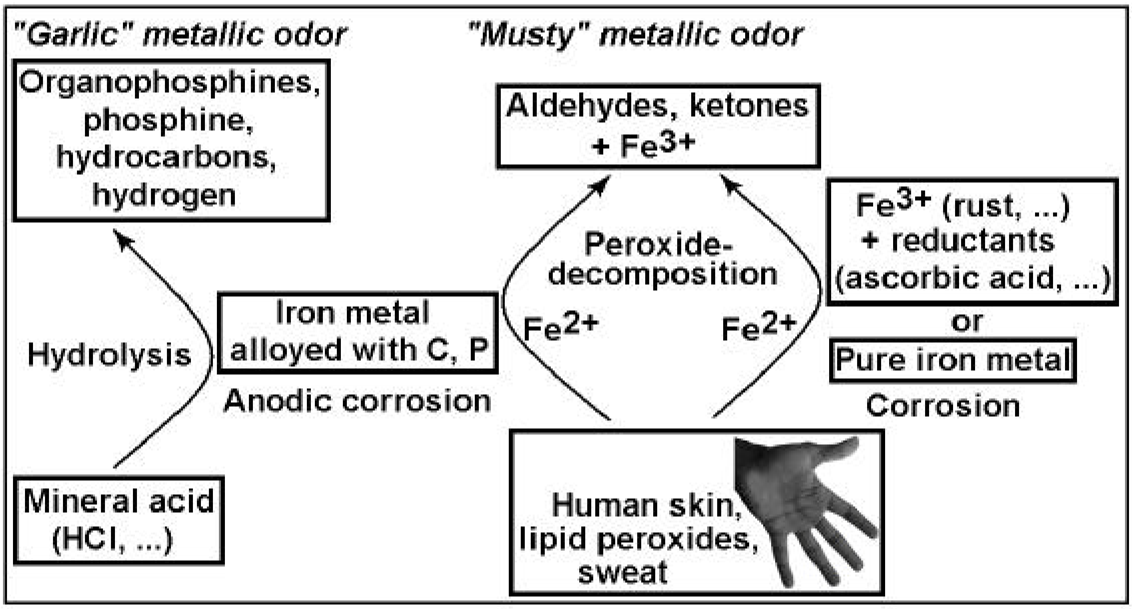
Iron metal Fe (0)	7439-89-6,	7439896
Ferrous ion Fe^{2+}	15438-31-0,	15438310
Copper metal Cu (0)	7440-50-8,	7440508
Cuprous ion Cu^+	17493-86-6,	17493866,
Brass	12597-71-6,	12597716
Zinc metal Zn (0)	7440-66-6,	7440666
Zinc ion, monovalent Zn^+	15176-26-8,	15176268
1-Octen-3-one (OEO),	4312-99-6	4312996
Hexanal	66-25-1,	66251
Heptanal	111-71-7,	111717
Octanal	124-13-0,	124130
Nonanal	124-19-6,	124196
Decanal	112-31-2,	112312
Phosphine, PH_3	7803-51-2	, 7803512
Methylphosphine	593-54-4,	593544
Ethylphosphine	593-68-0,	593680
Dimethylphosphine	676-59-5,	676595
Trimethylphosphine	594-09-2,	594092
Methylarsine	593-52-2,	593522
Dimethylarsine	593-57-7,	593577
Hydrogensulfide, H_2S	7783-06-4,	7783064
Methylphosphinic acid	4206-94-4	4206944
Methylphosphonic acid	25588-92-5	25588925

Comment on the title picture in the printed Table of Contents of „Angewandte Chemie“

The idea of the title picture with Roman emperor Vespasian on a coin sniffing a coin is based on a well-known historical joke summarized in Latin *pecunia non olet*, “money doesn’t stink”, or rarely *aes non olet*, "copper doesn't smell". Vespasian was answering his son Titus’s objection to his tax on public lavatories; holding a coin to Titus’s nose and being told it didn’t smell, he replied: Atqui e lotio ext (“Yet that’s made from urine”) (The Oxford Dictionary of Quotations, (c) Oxford University Press 1999). More exactly, this joke is reported by Roman historian Suetonius, (Suetonius: De Vita Caesarum--Divus Vespasianus, c. 110 C.E., chapter 23.3): “Reprehendenti filio Tito, quod etiam urinae vectigal commentus esset, pecuniam ex prima pensione admovit ad nares, sciscitans num odore offenderetur; et illo negante; ‘Atqui’, inquit, ‘e lotio est.’. (When Titus criticized him because he had even contrived a tax on urine, he held up some money from the first payment to his son’s nose, asking whether he was offended by the odor; and when he said “No”, he replied “Yet it comes from urine”)”.

Economists like to use this joke that money does not smell. However, we as sensory scientists disagree with the joke because certain metal coins have actually odor (“Metallic” is recognized as “an aromatic associated with metal coins”, ASTM E1627, 1997). In modern time, coins contain alloyed iron and copper. These two elements are important candidates that can be linked to metallic smell.

The printed paper in “Angewandte Chemie” shows two chemical mechanisms that cause two different smells of iron metal and its common alloys (Summary in **Supporting Figure S1**).



Supporting Figure S1: Schematic of the proposed two different iron odors: The “musty” metallic odor is caused by carbonyl hydrocarbons (aldehydes and ketones) that have their source in the reaction of skin lipids with ferrous ion. The “garlic” metallic odor is caused by organophosphines that have their source in C and P impurities alloyed with iron metal.

Part 1) Ironically, “in a touch of iron”, iron odor on skin contact is a type of human body odor (Methods, additional data and additional discussion)

Materials: Iron alloy plate standards (used for **printed Figure 2, printed Table 1**) were from Breitlaender, Germany, and their impurities are described in **Table 1 and Table S1**. Ultra pure iron was a powder from Alfa (no. 943001). Stainless steel type 316 is from a machining shop. Artificial sweat (pH 4.7, 0.7 N chloride) was prepared according to ISO standard 3160/2 (20g/L NaCl, 17.5g/L NH_4Cl, 5g/L acetic acid and 15g/L lactic acid with the pH adjusted by NaOH). Chloride (as in this sweat standard) plays an important role in accelerating the corrosion of iron, (and of copper, and brass) in near neutral solution, and stabilizing low-valence unstable intermediates during partial anodic metal dissolution as complexes ($FeCl^+$, $CuCl^{2-}$). Solutions of iron salts ($FeCl_2 * 4 H_2O$ and $FeCl_3$, analytical grade from Sigma-Aldrich) were freshly prepared in artificial sweat or water. Standards of C_6 to C_{10} n-alkanals, and 1-octen-3-one were from the Flavor and Fragrance Catalogue of Sigma-Aldrich (no. W351504). The metal samples and all glassware were carefully degreased with methanol/dichloromethane prior to use to avoid positive blanks of hydrocarbons by contamination with human skin or food lipids.
Non-iron metals: Selected experiments used ultra pure copper powder (99.999 %, Sigma-Aldrich no. 20,312-2), ultra pure zinc powder (99.9999%, Alfa no. 00694), ultrapure aluminium powder (99.9997%, Johnson-Matthey lot no. C17C17, filings from an ingot), ultrapure cobalt powder (99.9985%, Alfa no. 921001), ultrapure nickel powder (99.999%, Alfa no. 957001), ultrapure magnesium powder (99.98%, Alfa no. 998002), ultrapure tungsten powder (99.999%, Alfa no. 976475), brass (bar from a machining shop, or laboratory key), and gold (99.9%, bar from DEGUSSA).

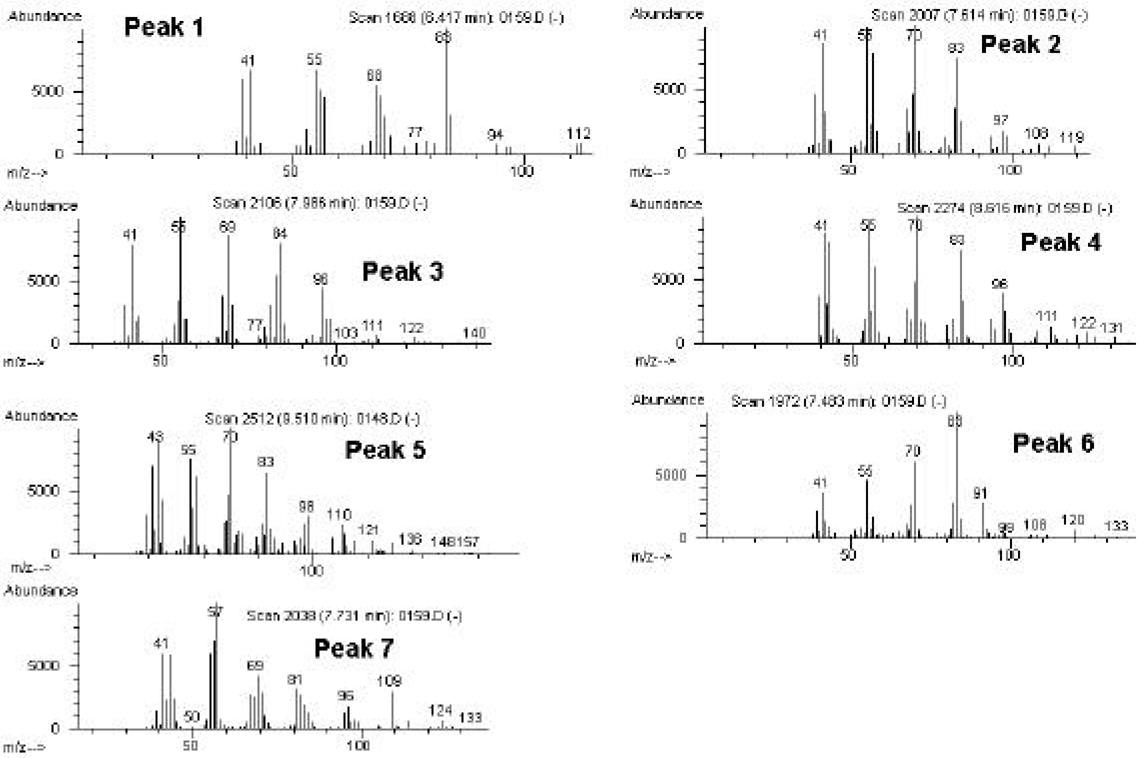
Contact of skin with ferrous ion or metals and production of odors: Intact skin (0.31 dm^2 palm skin or body skin in healthy natural state) of human subjects was treated with different forms of iron. Ferrous or ferric solutions (150 µL, up to 50 mM) were individually spread onto the skin. Ultra pure iron metal powder (up to 1 mmole) was spread and rubbed onto skin or iron metal plates (ca. 0.2 dm^2) were placed for up to one minute on skin pre-moisturized with 150 µL of artificial sweat. The iron-treated skin area was then tightly covered for five minutes by a glass funnel (covering 0.31 dm^2, volume of headspace 0.06 L), to accumulate the formed volatile compounds. For each iron treatment sample, a new and unused skin area was chosen. Treated skin areas were not used again for at least two days to allow for recovery of the skin-potential to produce metallic odor. The skin-contacted iron plates used were also used as samples, by covering them with a glass funnel. A SPME fiber (Supelco no. 57310-U) was inserted in the funnel for five minutes to collect volatile compounds for GC-analysis (see image embedded in printed **Figures 1** and **2**).

The quantity of ferrous iron released by the corrosion of the iron metal on contact with artificial sweat/skin was measured by using the common colorimetric FerroZine-assay, and the RSD of the method was 10 %.
Sensory testing of iron-skin-metallic odor adopted the Flavor Profile Analysis (FPA) sensory evaluation method (ASTM, STP 435) to train panelists and assess odors. Seven human subjects sniffed the treated skin and iron plates upon removal of the funnel. The odor was described by its tone (metallic, soapy, etc.) and intensity. All panelists were trained by using Fe^{2+} solution on skin to recognize the iron-skin metallic odor. The Virginia Tech Institutional Review Board approved the protocol.

Analysis of individual carbonyl hydrocarbons by SPME-GC/MS and SPME-GC-olfactometry (GC-O). Immediately after skin-metal contact, the SPME fiber collected volatile compounds for 5 minutes. The SPME samples were analyzed by GC/MS (Agilent GC column DB-5, 30 m x 250 µm x 0.3 µm, GC 6890, MS 5973, in EI mode, Environmental Chemstation G1701CA). SPME samples were also analyzed by GC-O with an equal GC and parallel detection by FID and Olfactometry (SGE ODO-2) and trained human subjects described the odor of separated compounds which were identified by FID detection and retention index. The RSD of the whole method was in the order of 25 %.
Typical SPME-GC/MS chromatograms of skin-borne carbonyl hydrocarbons are shown in **printed Figure 1** and similar **Supporting Figures S3 to S5**. Full scan data were obtained, but the chromatograms show a trace of m/z 55, which is a typical ion for aldehydes and ketones.

The peak areas for **printed Figure 1** (normalized for the largest peak of nonanal, 100%) are shown in **Supporting Table S1**. Identification of highly abundant C_6 to C_{10} n-alkanals and of key odorant 1-octen-3-one (**printed Figure 1**) was based on comparison with their standards analyzed by SPME-GC/MS and SPME-GC-O.

Identification of less abundant peaks enumerated 1 to 5 adopted Kovats Retention Indices (source: http://www.flavornet.org/d_kovats_db5.html) and comparison with NIST library mass spectra with at least 50% spectral match quality (**Table S1)**. The peaks 6 and 7 could not be identified as a reasonable spectral match compound. Peak BL like "Base Line" (6-methyl-5-Hepten-2-one, 90%) is a typical human skin ketone that is also available in control samples without iron, and is known as an attractor of mosquitoes (Lit. Cork, A. and Park, K. C. Identification of electrophysiologically-active compounds for the malaria mosquito, Anopheles gambiae, in human sweat extracts. *Medical and Veterinary Entomology*. **1966**, *10*, 269-276).



Supporting Figure S2: Mass spectra of minor peaks enumerated 1 to 7 in printed Figure 1 (similar to supporting Figure S3-b)

Supporting Table S1: Peak areas and evaluation of the importance of individual odorant peaks in printed Figure 1 (similar to supporting Figure S3-b)

Peak label (see printed Fig. 1)	Retention time, min	Compound of closest spectral match, and match quality (%)	Area of peak (% of maximum peak)		Odor detection threshold (ODT) (Rychlik *et al.*) µg/m^3		Odorant importance	Odor descriptor (Rychlik *et al.*)
			mass 55 trace	Total, TIC	range	minimum	Area % (TIC) / ODT (min)	
Hexanal	3.61	(Standard)	7.94	12.33	30-53	30	<0.1	Tallowy, leaf
Heptanal	5.61	(Standard)	15.66	12.46	250	250	<0.1	Fatty
1-Octen-3-one	6.67	(Standard)	25.77	4.6	0.03-1.12	0.03	153	Mushroom, metallic
Octanal	6.99	(Standard)	53.87	47.44	5.8-13.6	5.8	8	Fatty
Nonanal	8.09	(Standard)	100	100	4.5-12.1	4.5	22	Tallowy, fruity
Decanal	9.02	(Standard)	67.13	66.91	1	1	67	Orangeskin, flower
1	6.41	(*E*)-2-Heptenal, 50%	1.1	0.58	52.5-250	52.5	<0.1	Fatty, almond
2	7.61	(*E*)-2-Octenal, 78%	2.35	1.2	47	47	<0.1	Fatty, nutty
3	7.98	(*E*)-4-Nonenal, 83%	15.79	8.92				
4	8.62	(*E*)-2-Nonenal, 50%	1.77	1.11	0.1-3.6	0.1	11	Tallowy, cucumber
5	9.51	(*E*)-2-Decenal, 72%	0.52	0.4	3.6-4.9	3.6	<0.1	Tallowy, orange
6	7.48	no ID, RT=7.48 min	4	2.54				
7	7.73	no ID, RT=7.73 min	9.07	4.42				
BL	6.77	6-Methyl-5-hepten-2-one, 90%	11.65	7.72	50	50	<0.1	Fruity, floral

Evaluation of 1-octen-3-one (OEO) as a key odorant, by using SPME-GC-MS peak areas and literature odor thresholds

Two factors that determine the relative importance of an odorant in a mixture are its concentration (peak area) combined with its odor detection threshold concentration. The relative importance of individual odorant peaks in **printed Figure 1** for overall odor is approximated “semi-experimentally” by dividing their quantity (measured by the normalized % peak area (TIC)) by the literature based odor detection thresholds (ODT). To be consistent, ODT values from one single literature source (Lit. M. Rychlik, P. Schieberle, W. Grosch, Compilation of odor thresholds, odor qualities and retention indices of key food odorants. ISBN: 3-9803426-5-4, 1998) was choosen. The measurement of odor detection thresholds for these relatively high boiling and "sticky" odorants is very tricky, resulting often in too high ODT nominal concentrations. Therefore, the minimum ODT value from the literature range was choosen. It is evident that 1-Octen-3-one is the most important odorant (153.33 = 4.6/0.03). ODT numbers of 1-Octen-3-one are reported in the literature that are much lower (0.004 µg/m3) and that would increase its odor importance about tenfold, numerically.

Evaluation of 1-octen-3-one (OEO) as a key odorant, by SPME-GC-Olfactometry (GC-O) and by dilution olfactometry of the whole gas sample under the funnel:

GC-olfactometry (GC-O) is a method that allows human subjects to evaluate the “odor intensity” and “odor descriptor” of individual GC peaks. Since the peak areas and peak molar-quantities can be calculated from parallel FID detection (or by a parallel reproducible GC-MS experiment), and the peak areas can be manipulated to nearly undetectable levels, it is possible to assign each detectable peak an “odor detection threshold of the GC-peak”. Dilution olfactometry is another more common technique that can analyze the odor threshold of whole gas mixtures as a “dilution factor to odor threshold” (see a more detailed description of dilution olfactometry in the second part of Supporting Information).

Results of GC-O: The peak of 1-octen-3-one (OEO, CAS no. 4312-99-6) in a typical SMPE-GC-O sample was rated by human subjects to be by far the most odorous peak (musty-mushroom-metallic like odor). The “odor threshold of the OEO peak” was 0.5 pmole, while 23 +/- 12 pmole per OEO peak were measured in a typical SPME sample, which is 46 times above odor threshold by GC-O.

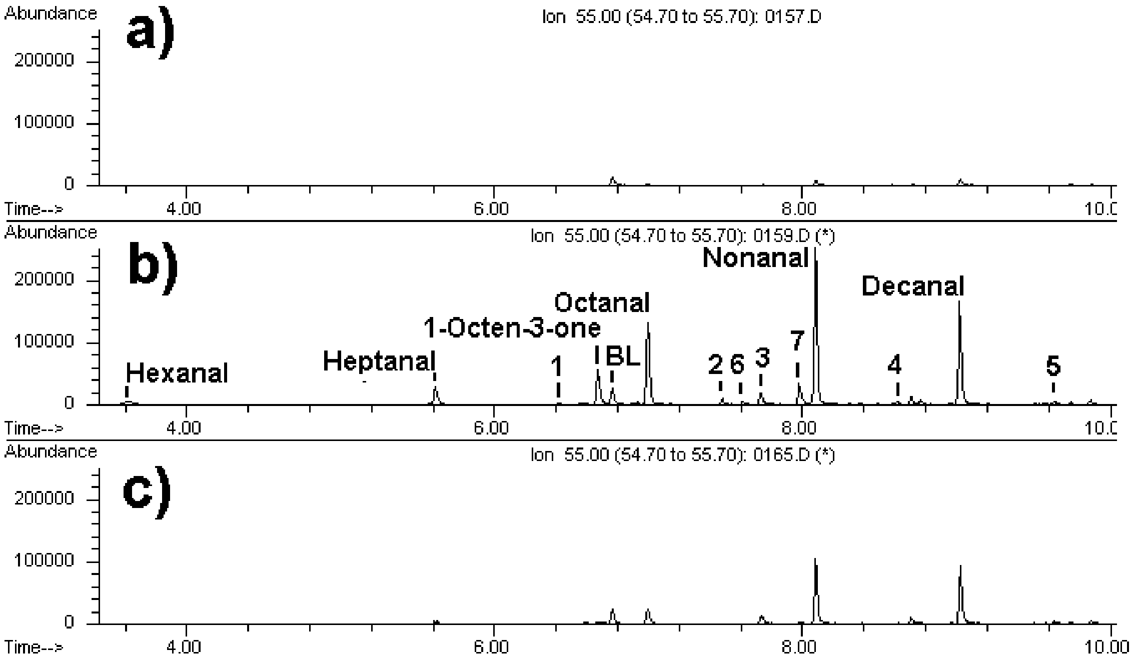
Results of dilution olfactometry: The concentration of the key odorant OEO in typical “whole” headspace gas above the skin was about 5 µg/m^3 or about 100 times above odor threshold measured by dilution olfactometry (0.05 µg/m^3). The dilution factor to the odor detection threshold of a typical whole gas mixture sample from under the glass funnel on skin was measured by dilution olfactometry and is in the order of 300. Thus, OEO is contributing about 1/3 (=100/300) of the total odor concentration of the complete headspace gas above skin on the touch of iron.

Quantification of the most abundant carbonyl hydrocarbons for printed Figure 2

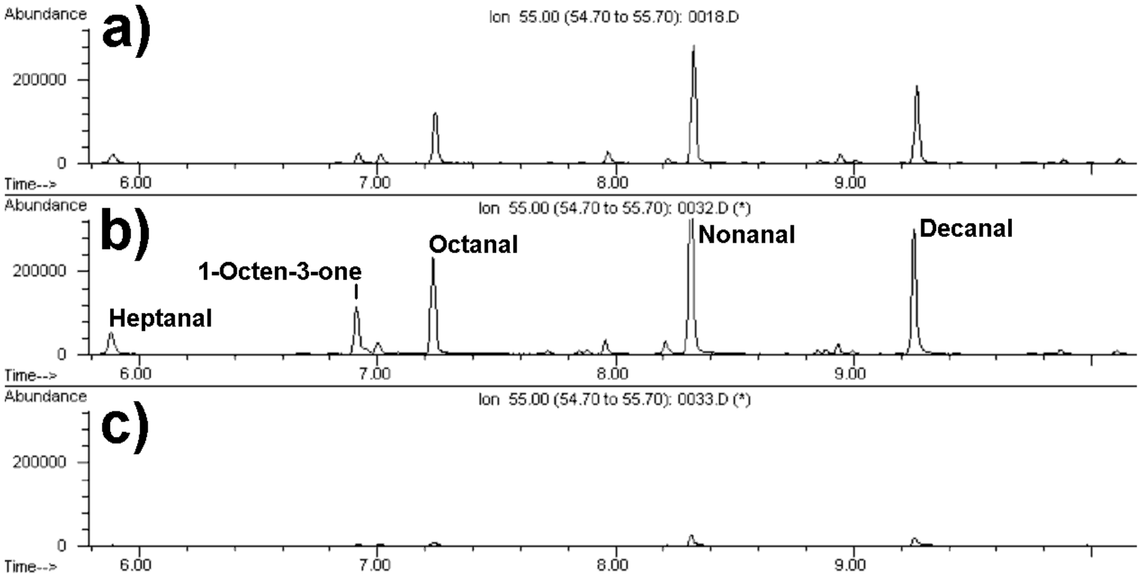
A straightforward quantification approach for SPME-GC/MS data presentation was adopted: A sum $\mathbf{n_{fiber}}$ of the nmole-amounts of the key compounds C_6 to C_{10} n-alkanals and 1-octen-3-one on the SPME fiber was calculated from their GC peak areas by comparison with peaks of standards in methanol. A typical distribution of the important peaks C_6 to C_{10} n-alkanals and 1-octen-3-one on the SPME fiber was 73, 48, 234, 407, 140, 24 pmole, resulting in a sum of 926 pmole. Thus, typical high metallic odor resulted in a sum $\mathbf{n_{fiber}}$ ~ 1 +/- 0.2 nmole hydrocarbons (when measuring skin of the same person). A total nano-molar amount $\mathbf{n_{skin}}$ of these hydrocarbons generated per dm^2 of skin (reported in **printed Fig. 2**) was estimated according to equation S1:

$$\mathbf{n_{skin}} / dm^2 = \mathbf{n_{fiber}} * 100 / 0.31\ dm^2 \qquad (\mathbf{S1})$$

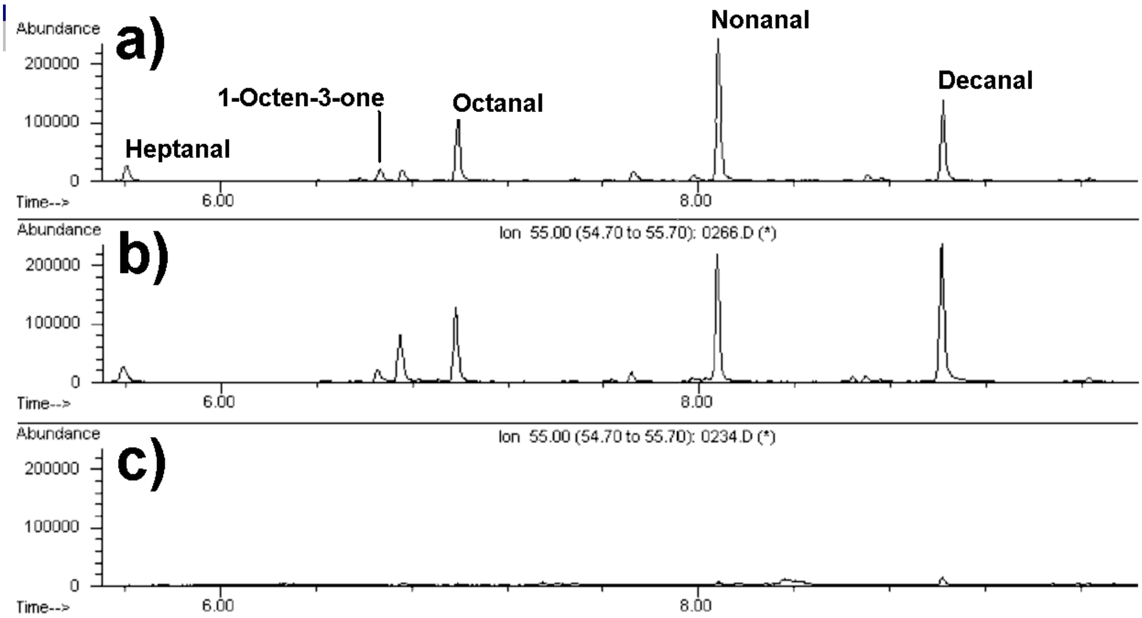
The empirical factor 100 is akin to an equilibrium constant “skin-air” of odorants, and is based on additional model experiments that show that the SPME fiber adsorbed about 1% of the total amount of the hydrocarbons (details not shown). The number 0.31 dm^2 is the actually analyzed skin area covered by the glass sampling funnel.



Supporting Figure S3: SPME-GC/MS trace of carbonyl hydrocarbons from human haired body skin with addition of a) no iron as control b) ferrous chloride solution, 150 µL, 10 mM c) blood, 0.1 mL. The figure shows the similarity of blood-iron and ferrous ion in odorant formation. The peak **BL, or base line, describes a compound always present in skin and tentatively identified as 6-methyl-5-hepten-2-one.**



Supporting Figure S4: SPME-GC/MS trace of carbonyl hydrocarbons from human palm skin, with addition of 150 µL of a) 10 mM $FeCl_2$ b) 10 mM $CuCl_2$ + 100 mM ascorbic acid c) 150 µL of 10 mM $CuCl_2$. The figure shows the similarity of ferrous iron and cupric ion/ascorbic acid (reduced to cuprous ion), in odorant formation.



Supporting Figure S5: SPME-GC/MS trace of carbonyl hydrocarbons from human haired body skin on contact with a) ultra pure iron powder b) ultra pure copper powder, c) control with no metal added. The figure shows the similarity of iron metal and copper metal, in odorant formation.

Between-person comparison of levels of carbonyl hydrocarbons: Similar levels of carbonyl formation were found for 6 other human subjects; the intensity of metallic odor for ferrous solutions contacting palm skin was rated “moderate” by the human subjects. Significant between-person differences in production of carbonyls were observed when a steel plate contacted dry palm skin *without* artificial sweat (4 human subjects, 110 +/- 116 nmole/dm^2), but the relative distribution and odor description was similar. Metallic odor was higher at low palm pH (between-person range 4.5 to 6.5) and high sweating. When the experiment was repeated by adding artificial sweat to the palm before contact with steel, this increased iron corrosion and carbonyl formation and minimized differences between subjects (253 +/- 116).

Model experiments with typical unsaturated skin fatty acids, with animal skin, and ferrous iron: Model experiments applied ferrous ion solution to unsaturated fatty acids that are typical of the human skin epidermis (arachidonic acid, CAS no. 506-32-1, Sigma no. A9673; linoleic acid, CAS no. 60-33-3) and skin sebum wax (oleic, CAS no. 636-34-0, Sigma no. O1008). The acids were diluted by a factor of 10 in methylacetate. 0.5 mL of the solution was separately applied to a 50 mm glass filter disk on an agar plate. Before and after 6 hours of air exposure, the disks/acids were amended with 0.4 mL of 10 mM ferrous chloride in water, evaluated by a sniff test and analyzed by SPME-GC/MS.

"*Live*" pig skin (up to one hour post mortem, from a slaughter house) contacted with ferrous iron resulted in a "pure" metallic odor very similar to live human skin. "*Dead*" pig skin ((48 hours post mortem and after scalding), pork (from a food market), and typical polyunsaturated skin fatty acids (e.g., arachidonic, oleic, and linoleic), after air-oxidation and ferrous iron addition, formed a different meaty, fatty-metallic "oxidized food" odor. The same major carbonyl hydrocarbons were detected, but the relative **distribution** of individual hydrocarbons was very different than that of live human skin.

An artificial mixture of the n-alkanales and OEO was prepared in water and applied to 50 mm glass filter disks on an agar plate that resulted in similar SPME chromatogram as in printed Figure 1. The odor of the headspace above the agar plate was more fatty-metallic than the odor produced from iron-skin contact..

It was not the scope of this project to completely recreate the metallic odor of iron and skin by model systems with mixed fatty acids or with carbonyl hydrocarbon mixtures. Many trace compounds have very low odor thresholds as we demonstrated for OEO. Compounds may be present at much lower concentration than OEO and could "modulate" the overall odor. SPME might also not capture important low-boiling volatiles: Occasional analyses of the whole headspace gas under the funnel by cryo-trapping GC/MS yielded large peaks of acetaldehyde, acetone and other low boiling carbonyl hydrocarbons from ferrous ion treated skin (data not shown).

Analysis of metallic blood-skin-odor: In a self-experiment, the first author rubbed his leg skin with 0.1 mL of his own blood (taken by using commercial sterilized lancets). SPME GC/MS analysis of gas samples from skin under the glass funnel resulted in 78 +/- 7 nmole/dm^2 carbonyl hydrocarbon formation, compared to 311 +/- 56 with addition of 1500 nmole ferrous ion solution, 4 +/- 0.4) with addition of blood plus 10 mM FerroZine as iron-neutralizing chelator, and 11 +/- 8 with addition of artificial sweat only as control (N = 4) (**Supporting Figure S3-c)**). Animal blood (pig, slaughterhouse) resulted in similar metallic odor. ,

Anecdotal evidence was collected that the human population is linking metallic odor (scent) to blood: A Google search (1400 hits "metallic scent", 952 hits "metallic scent" AND blood, 721 hits "metallic scent" AND vampire, of Feb. 17, 2006) revealed that "metallic scent" is a recognized sensory descriptor that is often linked to spilled blood. Although, the evidence originates mostly from fiction and from obscure sources, a Google search is a way to capture such statistical "sensory information" that is otherwise not easily producible by regular science.

Comparison of iron metal with other metals (copper, brass, zinc etc.): When solid copper metal or brass (copper-zinc alloy) was contacted with the skin instead of iron, a similar metallic odor and GC-peak pattern of carbonyl hydrocarbons was produced and up to one µmole/dm^2 of monovalent cuprous ion was detected as a corrosion product (**Supporting Figs. S3 to S6**). Zinc, a metal that forms Zn^{2+} but no stable Zn^+, was hesitant to form metallic odor, except on very strong rubbing of the metal versus skin (that could produce metastable monovalent Zn^+). The use of common color-tests to demonstrate directly on human palm skin the presence of low-valence ion (ferrous and cuprous) from the corrosion of iron, copper and brass alloys is shown in **Supporting Figure S6**. Alumina powder rubbed on skin did not produce significant odorants.

These results provide additional evidence that it is not metal evaporation, but skin lipid peroxide reduction and decomposition by low valence metal ions that produces the odorants.

Table S2 shows an overview of the potential of different metals and control materials to produce metallic odor in contact with human skin of one person. Aluminium is an example of metals that do not cause metallic odor.

Supporting Figure S6: Colorimetric quick-test for low-valence ion corrosion products of metals after one minute of contact with human palm skin of one author, and artificial sweat. Left: Ultra pure iron powder + ferrozine reagent solution, magenta color by ferrous (low-valent Fe^{2+}) ion complex. Similar results are obtained with samples of cast iron and steel. Middle and right: US Copper penny and brass key, plus bathocuproine reagent solution, orange color by cuprous (low-valent Cu^{+}) ion complex. Similar results are obtained with samples of ultra pure copper.

Table S2. Comparison of carbonyl and metallic odor formation when different metals are rubbed on skin. Values from equation S1. Quartz sand was used as a control whether simply its mechanical action on skin could trigger metallic odor. H_2O_2 was tested whether simply its skin oxidation power could trigger metallic odor. Analysis of additional metal powders (data not shown) was limited to rating of metallic odor (Cobalt 99.9985%, weak; Nickel 99.999%, no; Magnesium 99.98%, no; Tungsten, 99.999%, weak, gold, 99.9% no).

Skin treatment	Carbonyl hydrocarbons on skin nmole / dm^2 skin				Rating of metallic odor
	Average	Min	Max	N	
Steel 165H	267	192	309	3	medium
Cast Iron 661/3	247	177	315	3	medium
Iron ultrapure (6.0)	203	154	242	3	medium
Stainless steel 316	56	33	75	5	weak
Copper ultrapure (5.0)	246	228	277	3	medium
Zn ultrapure (6.0)	71	18	191	4	weak
Al ultrapure (5.0)	34	18	72	4	no
Quartz sand	6	5	8	3	no
H2O2, 3%	4	4	5	2	no

Part 2: Pickled iron – C-P-alloyed iron attacked by acid develops organophosphines with "garlic" metallic odor (Methods, additional data and additional discussion)

Materials: Certified alloy plate standards of high phosphorus engineering iron ("white" cast iron), carbon/low alloy steel and alumina (Breitlander GmbH, Hamm, Germany) with the impurity described in **Supporting Table S3** were used for the sniff tests and to produce filings for HCl dissolution. Ultra pure iron was from Alfa (no. 943001). Ultra pure HCl and NaOH (Merck, Darmstadt) and Millipore water was used as reagents. Durable compressed gas standards of 1000 ppmv phosphine (PH_3), methylphosphine (CAS 593-54-4), dimethylphosphine (676-59-5), methylarsine (593-52-2), and dimethylarsine (593-57-7) in nitrogen (Messer Griesheim, Duisburg, Germany) were used to prepare diluted work standards. A compressed gas standard of 100 ppmv C1 to C6 n-Alkanes was used to calibrate ICP-MS for volatile carbon compounds.

Supporting Table S3: Composition of the certified metal standards used for printed Figure 2 and printed Table 1 of the publication.

	%	µg/g (= % x 10^4)						
Metal standard / alloy	Fe	Cr	Mn	Si	C	P	As	S
Cast iron SCRM 665/3	95	10000	1800	16000	32100	11100	4	500
Cast iron SCRM 661/3	95	10000	4100	31500	26300	8300	8	680
Cast iron SCRM 664/3	95	10000	6200	28400	29200	5500	7	1200
Cast iron SCRM 662/3	96	10000	8100	23700	30400	2500	7	870
Cast iron SCRM 663/3	95	10000	10400	20200	34900	1030	4	290
Steel CKD 165 H	97,2	1700	16300	2200	1500	890	200	130
Steel CKD 162 H	99,5	200	1000	1400	200	50	40	20
Iron, ultra pure	99,9987				<10	<1		
Aluminium 122/03	0,059	180	160	380	<10	75	53	
Aluminium 124/03	0,13	530	490	930	<10	1	0	

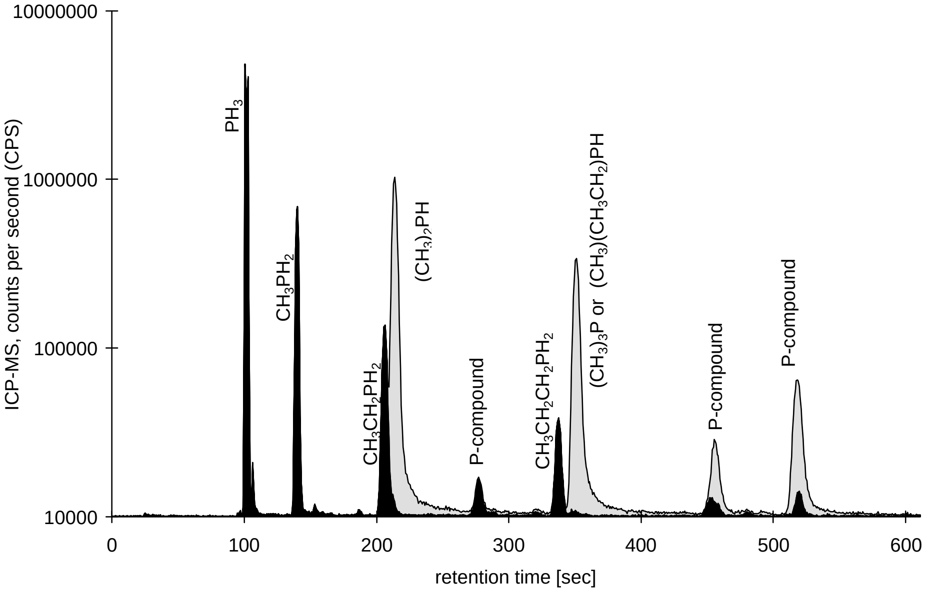
Preparation of odor samples: Samples for preliminary odor tests were produced by placing a plate of the cast iron standard for one minute either onto human skin or onto the bottom of a glass agar plate that was moistened with the acidic reagent (artificial sweat or 0.01 N HCl). The sniff test on the acid treated plate took part within 5 seconds after removal from the reagent, before the odorants faded away (oxidized). Subsequent tests used the metal and HCl only, because skin is not source of this type of metallic odor.

Odor samples for additional preliminary GC-NPD analysis were produced by placing a piece of the iron 661/3 into a 100 mL all glass syringe with 1 mL of 1 N HCl. The sniff test used headspace gas directly pushed out of the syringe. The odor was garlic-carbide-like, and GC-NPD showed a small peak with the retention time of methylphosphine. However, the concentration of the oxygen-sensitive organophosphines was not high enough, to work their way through the oxidizing surface of the analytical GC-MS and GC-ICP equipment, and of an olfactometer, and could not be detected by these methods.

Samples of metal that were sufficiently concentrated for both chemical analysis and dilution olfactometry (used for **printed Table 1**, **Supporting Figures S7 and S8**) were produced by rapid dissolution of 5.6 to 56 mg of iron (27 mg aluminium) filings from the metal plates, in 3 mL of 1 N HCl at 100 ^oC for 5 min in an anoxic closed glass-bubbler with a magnetic stirrer. The evolved gas samples for GC analysis were completely purged off the metal with helium, cryotrapped, cryofocussed, and separated on a 30 m x 0.32 mm 5 µm CP-Sil5CB GC column (Chrompack). The purge and trap analysis was then repeated after the pH of the reaction mixture was increased from pH 0 to pH 14 by adding 5 mL of 1 N anoxic NaOH to purge out the more alkaline secondary and tertiary organophosphines. The similar gas samples for olfactometry were produced by combining the gases from the reaction solution at pH 0 and pH 14.

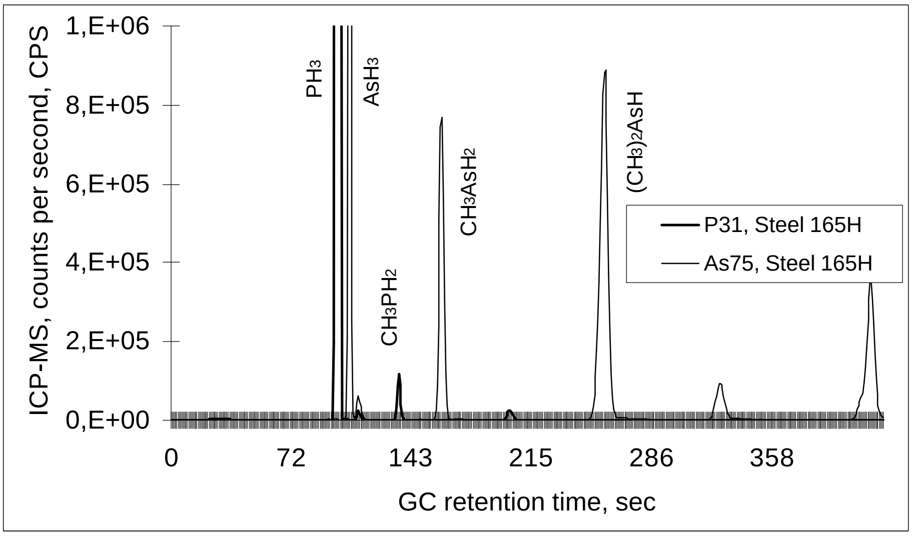
Chemical analysis of the volatile phosphines and hydrocarbons in **printed Table 1** used Inductively Coupled Plasma ICP/MS (Perkin-Elmer Corp. "ELAN 5000", graphics mode). The mass of volatile phosphines (hydrocarbons) per unit mass of metal (**printed Table 1**) was determined from the GC/ICP/MS P-31 (C-13) trace peaks areas after comparison with the peak area of a PH_3 (butane) gas standard (Messer-Griesheim, Duisburg, Germany). Additional detectors (GC/Quadrupole-MS (HP), GC/Ion trap-MS (Varian, "Saturn"), GC with parallel phosphorus detectors NPD/FPD (HP)) were used to verify the chemical identity and quantity of the phosphines by comparison with mass spectra of the NIST database (National Institute of Technology, US) and with mass spectra of the gas standards of methyl- and dimethylphosphine. The organoarsines (**Supporting Figure S8**) were also identified by GC/Ion-Trap-MS (Varian, "Saturn"). Out of a plethora of hydrocarbons in the gas samples, dienes and acetylenes were identified by comparison with mass spectra of the NIST database. All analyses were performed in duplicate (RSD of the whole procedure 25 %).

Example GC/ICP-MS chromatograms of the gas product of HCl dissolution of iron metal are presented in **Supporting Figure S7** (phosphines from cast iron) and in **Supporting Figure S8** (phosphines and arsines from low alloy steel).



Supporting Figure S7: GC/ICP-MS P-31-traces of organophosphines and of phosphine(PH3) evolved from 5.6 mg filings of cast iron 661/3 on HCl dissolution*

*PH_3 phosphine, CH_3PH_2 methylphosphine, $CH_3CH_2PH_2$ ethylphosphine, $(CH_3)_2PH$ dimethylphosphine, $CH_3CH_2CH_2PH_3$ propylphosphine, $(CH_3)_3P$ trimethylphosphine, $(CH_3)(CH_3CH_2)PH$ methylethylphosphine. Black areas represent PH_3 and weakly basic monoalkylphosphines, shaded areas are strongly basic di- and trialkylphosphines



Supporting Figure S8: GC/ICP-MS traces of phosphines and arsines evolved from 56 mg filings of low alloy steel 165H on HCl dissolution*
*PH_3 phosphine, CH_3PH_2 methylphosphine, AsH_3 arsine, CH_3AsH_2 methylarsine, $(CH_3)_2AsH$ dimethylarsine. The cause of the methylarsines is the high arsenic content of this steel 165H (see **Table S3**)

Olfactometry testing of the odor intensity and description of the samples: The samples were reaction gas of metal dissolution in HCl (united gas fractions purged off the reaction solution at pH 0 and subsequently at pH 14) and diluted certified standards of CH_3PH_2 and $(CH_3)_2PH$. Each sample was analyzed three times by olfactometry with a trained panel of four human subjects and a TO7 olfactometer, Mannebeck, Kiel, standard procedure VDI-RL 3881 and 3882. Olfactometry is a method to estimate the odor concentration of a gas sample. During olfactometry, human subjects used their noses to determine if a test gas sample diluted with air has an odor. They started with an infinitely diluted sample (clean air), and reported when on stepwise less dilution the odor becomes barely detectable (odor detection threshold) and subsequently can be recognized by a descriptor (at or above odor recognition threshold). This dilution made also sure, that the concentration of toxic phosphine remained below safety limits.
To measure the relative odor concentration of the gas samples of mixed composition from HCl-dissolved iron, olfactometry used simply the dilution factor of the sample at the odor detection threshold. As an example, the complete gas sample of HCl dissolution of 5.6 mg of cast iron 661/3 was diluted with nitrogen in a Tedlar bag to a final volume of 5 liter. Olfactometry yielded for this sample a dilution factor to odor threshold of 40,000 (respectively 46 dB +/- 2 dB). That translates into an absolute dilution volume at odor threshold of 40,000 times 5 liter or 200 m^3 for 5.6 mg dissolved iron, or the 35700 m^3 per g iron 661/3 that are reported in **printed Table 1** of the publication. In other words, the gas product of dissolution 1 g cast iron 661/3 can be diluted to 35700 m^3, before its odor becomes undetectable. Here, the unit m^3 is akin to “OU” (odor unit, the amount of odorant(s) present in one cubic meter of odorous gas (under standard conditions) at the panel threshold. See also "European Odor Unit"). Thus it could also be stated that one g cast iron 661/3 releases on HCl dissolution odorants that make up 35700 odor units.

To measure the odor threshold concentration of the available key odorant standards methylphosphine and dimethylphosphine (6 and 3 ng P / m^3), olfactometry was also used. As an example, olfactometry yielded for a gas standard of 0.1 ppmv (1 of 10 million) dimethylphosphine (DMP) in nitrogen a dilution factor to odor threshold of 40,000. That translates into a dilution factor at odor threshold of 40,000 times 10 million, equal to 400 billion, for pure dimethylphosphine. That translates into a chemical concentration at odor threshold of $(400\text{ billion})^{-1}$ m^3 DMP / m^3 air, or 4 pptv or the reported 3 ng P /m^3 air (1 nL DMP contains ca. 1.2877 ng element P). A diluted PH_3 standard was tested by an author only, and proved to have a much higher odor detection threshold above one ppmv, respectively ng/m^3.

To describe the odor of the same gas samples, the same 4 human subjects selected descriptors from a given list (key/coin, calcium carbide, garlic, organic, musty, rotten, sour, sweet, acrid, wood, cement, fruity, bakery, fecal). They were trained to recognize the smell of calcium carbide from BUNA/Schkopau, and were otherwise unprepared. Each subject described each sample on three olfactometry tests, and was forced to assign for each test three crosses to the list of descriptors (for example 1 cross “carbide”, 1 cross “garlic” 1 cross “cement” if all three descriptors are subjectively prevalent, or 3 crosses “garlic” if only “garlic” was prevalent etc.). For evaluation of the data, for each descriptor was assigned a “percent importance” value. For example, if 36 crosses (4 subjects x 3 tests x 3 crosses) were made for cast iron 661/3, and 14 of them assigned to the descriptor "garlic", the importance value of "garlic" is 14 of 36, or 39%. The results of all samples are listed in **Supporting Table S4**. This table allows the conclusion in the paper, that odor from HCl dissolved cast iron and steel smells garlic-carbide like. The descriptor “garlic” was also significantly chosen for gas of dissolved aluminium 122, likely because it contained the volatile metal hydrides SiH_4, PH_3, AsH_3, SbH_3, and BiH_3 (data not shown).

Supporting Table S4: Percent importance of olfactory descriptors of gases evolved on dissolution of metals and comparison with typical organophosphines. Descriptors garlic, calcium carbide and cement are prevalent. Descriptors fruity, fecal, sweet, organic, musty, bakery were very rarely selected and were omitted from the table, but they are part of the sum of 100%.

Gas sample (gas standard or gas from metal dissolution)	Garlic	Calcium-carbide	Cement	Acrid	Key/coin	Sour	Rotten	Wood	% Sum
Methylphosphine	**83**	9		8					100
Dimethylphosphine	**67**			22		3	8		100
Cast iron SCRM 661/3	**39**	**22**		8	11	12		8	100
Cast iron SCRM 662/3	**40**	**22**	14	8	8	8			100
Cast iron SCRM 663/3	**60**	**11**	3			8	8	6	100
Cast iron SCRM 664/3	**57**	**21**	8		3	8		3	100
Cast iron SCRM 665/3	**42**	**33**	4			9	8	4	100
Steel CKD 165 H	**26**	**29**	**22**	8		8		7	100
Steel CKD 162 H	**25**	**22**	**35**	7	3	8			100
Aluminium 122/03	**46**	3		10	8		25		100
Aluminium 124/03	**20**	2		6	36	18	18		100

Evaluation of organophosphines as key odorants from HCl dissolved cast iron: A total amount of 82 µg organophosphines arises from one gram of cast iron 661/3 filings dissolved in HCl (82 µg/g, see **printed Table 1**). The odor threshold concentration of each of the alkylphosphines diluted in air is assumed to be 0.003 µg/m^3 (set equal to the value measured for dimethylphosphine). The calculated air-dilution volume to the odor threshold of the organophosphine fraction in the gas product of HCl-dissolution of one g iron is equal to 82 µg/g divided by 0.003 µg/m^3 (that is 27290 m^3/g). The experimental dilution volume to the odor threshold of the whole reaction gas (HCl-dissolution of one g iron) with air is equal to 35700 m^3/g (see **printed Table 1**). Thus, the organophosphine fraction of one g cast iron 661/3 can make 27290 m^3 of air odorous, while the whole gas can make 35700 m^3 of air odorous; that is 27290/35700 or 3 quarter, of the total odor. This justifies the conclusion in the publication that organophosphines account for a significant fraction of the odor of the whole gas product. The difference of the odor of organophosphines and the whole gas sample can be explained by other gases, such as hydrocarbons (**printed Table 1**), arsine and organoarsines (**Supporting Figure S8**), and H_2S and organosulfides (data not shown).

The odor of dissolution of another cast iron-carbon (3%) alloy with no other elements resembles that of calcium carbide, and the odor from an iron-carbon(3%)-phosphorus(0.5%) alloy with no other elements resembles that of organophosphines.

Chemical analysis of methylphosphinic acid from rusting of cast iron

The analysis was carried out by the TNO Prins Maurits Laboratory, Project no: 214498010, Reference no: 98D1/2112, in accordance with the quality assurance criteria of the Netherlands Council for Accreditation (STERLAB). The following data originate from the project report that was provided by cooperation. Water extracts of rusted cast iron samples were analysed. using electrospray (ES) LC/MS and NMR. Quantitative LC-ES-MS produced the following amounts of methylphosphinic acid in mg per kg of iron:

- rusted standard 664/3 (description of iron 664/3 in **Table S3**, PML code 98ACS13): 0.45 and 0.41 mg/kg (duplicate measurements).
- rusted laboratory tripod (0.38% phosphorus, 2.8% carbon, PML code 98ACS14): 0.09 and 0.07 mg/kg (duplicate measurements).

(Additional chromatograms and spectra can be provided.)