Communications

The Two Odors of Iron when Touched or Pickled: (Skin) Carbonyl Compounds and Organophosphines**

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Humans are perplexed by the metallic odor from touching iron metal objects, such as tools, cutlery, railings, door handles, firearms, jewelry, and coins. Phosphorus-containing iron which is under acid attack gives rise to a different "carbide" or "garlic" odor which metallurgists have attributed to the gas phosphine (PH_3);[1–3] however, we found that purified PH_3 at breathable dilution has hardly any odor. The aim of our research is to understand the chemical causes of these two iron smells in our engineered metal environment.

1) Ironically, the iron odor on skin contact is a type of human body odor[4]

Seven human subjects sensed an immediate "musty" metallic odor when their palm skin touched a ferrous (Fe^{2+}) solution or metallic iron (ultra pure iron powder, steel, and cast iron plates) moistened with artificial sweat (pH 4.7 and 0.7 N chloride). The metallic odor was recognized on both the skin and on the metal plates. The test subjects agreed that this metallic odor was similar to that encountered in their life experience on smelling sweaty hands in contact with every-day iron objects. Ferric (Fe^{3+}) solution did not produce metallic odors.

Parallel chemical (SPME GC/MS) analysis (Figure 1, Supporting Information) of metallic-smelling gas samples from the skin of each human subject, after its contact with iron metal or aqueous ferrous ion, resulted in a reproducible distribution of highly abundant C_6 to C_{10} *n*-alkanals and at least five more minor peaks arising from unsaturated
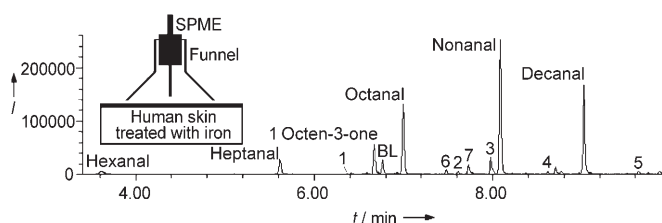
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Figure 1. Typical chemical fingerprint of carbonyl hydrocarbons produced by human haired body skin on the addition of iron. Aqueous FeCl$_2$ solution, 150 µL, 10 mM, 0.3 dm^2 skin, solid-phase micro-extraction (SPME) GC/MS trace for ion mass 55. Inset illustrates sampling procedure for measuring the volatiles by SPME. **1–7** = unsaturated carbonyl compounds. BL = baseline peak (unsaturated ketone also present in control samples of skin without iron). See Supporting Information.

aldehydes and ketones. GC-olfactometry and classical dilution olfactometry revealed 1-octen-3-one (CAS no. 4312-99-6, mushroom-like metallic odor, odor threshold near 50 ng m^{-3} [5]) as a key odorant that contributes about 1/3 of the total odor concentration (dilution factor to odor threshold ca. 300) of the complete gas sample above the skin under a glass funnel.

The quantity of the odorous carbonyl compounds (Figure 2) and the metallic odor increased with the quantity of Fe^{2+} (but not Fe^{3+}) ions in contact with the skin of one human subject, up to a relatively constant limit level near 300 nmol dm^{-2} carbonyl compounds above 1000 nmol dm^{-2} Fe^{2+} ions. The iron odor from UV-protected and unprotected haired skin (e.g., calf and thigh skin) and from palm skin was similar. Similar levels of carbonyl formation were found for the six other human subjects.
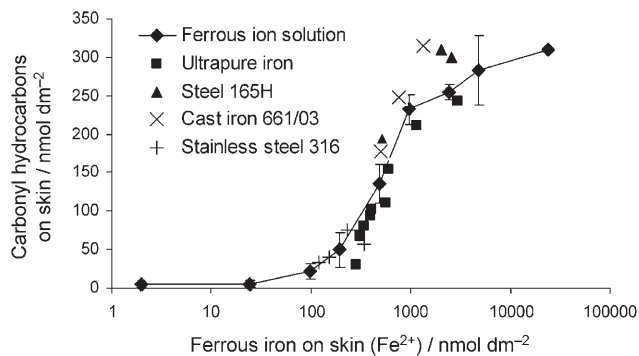
Figure 2. Molar amounts of carbonyl hydrocarbons formed by haired body skin of one human subject versus Fe^{2+} ion exposure. Fe^{2+} was either added as an aqueous solution or resulted from the corrosion of solid iron alloys in contact with skin and artificial sweat. For the impurity levels of the metals, see Table 1 and Supporting Information. Error bars indicate the low and high values of duplicate measurements. The corresponding concentration of the skin odor, measured as the dilution factor of the complete headspace gas (above the skin, under a glass funnel) to the odor threshold is approximately 300 (intensity rated moderate) at high Fe^{2+} ion exposure and approximately 10 without iron. Controls of iron alloys or an Fe^{2+} ion solution without skin, skin with artificial sweat but without iron, and skin with an Fe^{3+} ion solution produced diminishing levels of the hydrocarbon compounds, and the metallic odor was not detectable. Additional chemical reductants, such as ascorbic acid, regenerate Fe^{2+} from Fe^{3+} ions and increase the potency of small amounts of Fe^{2+}.

Odorant precursors: The molar quotient of Fe^{2+} ion reagent consumed and carbonyls (aldehydes) produced (Figure 2, below 1000 nmol dm^{-2} Fe^{2+}) is on the order of five, similar to a reported[6] quotient of Fe^{3+} produced and lipidperoxide decomposed by Fe^{2+}. The Fe^{2+}/xylenol-orange test[6] produced orange coloration of the skin and a metallic odor, indicating the formation of Fe^{3+} from Fe^{2+} and the reductive decomposition of the preexisting skin lipidperoxides into odorants. Lipidperoxides can be formed from a plethora of skin lipids,[7,8] through lipoxygenases[9] or oxidative stress (e.g. UV light). The limited supply of skin lipidperoxides explains the leveling of odorants at higher amounts of Fe^{2+} addition (Figure 2). The specific "pure" metallic odor of live skin and Fe^{2+} is explained by a certain distinct mixture of skin lipidperoxides which are the precursors to the odorants, and this mixture is different to the peroxide composition of "dead" meat (food) and oxidized unsaturated fatty acids that smell more "fatty".

Blood iron: Blood of one of the authors rubbed onto his own skin resulted in similar metallic odor and the same odorants (78 ± 7 nmol dm^{-2}, 4 repetitions) as in the above experiments. Controls by addition of FerroZine which is a blood-iron chelator suppressed the reaction (4 ± 0.4). Aerated and homogenized blood also developed metallic odor on its own. There are reports that blood iron[10] can decompose blood lipidperoxides and that FerroZine inhibits this reaction.[11] This finding confirms that blood iron can trigger the metallic odor on skin or in blood itself.

Overall "skin–iron odor" mechanism: The metallic odor from iron contacting skin is surprisingly a type of human body odor. Sweaty skin corrodes iron metal to form reactive Fe^{2+} ions that are oxidized within seconds to Fe^{3+} ions while simultaneously reducing and decomposing existing skin lipidperoxides to odorous carbonyl hydrocarbons that are perceived as a metallic odor. This fast reaction creates the sensory illusion that it is the "metal in itself" that we smell right after touching it. Similar mechanisms underlie the skin–metal odors of iron, copper, and brass (Supporting Information) used as every-day objects.

Based on these findings, the medical community should consider developing this Fe^{2+} test of skin, blood, body tissues, to identify specific fingerprints of volatile carbonyls as indicators of individual body odor, oxidative stress, and diseases. Utility engineers could explain cases of customer complaints of metallic odor and flavor of drinking water by the production of carbonyls: We found that in a kitchen situation, ascorbic acid in foods and water promptly reduces Fe^{3+} ions ("red" rust) in water to the "green" Fe^{2+} form that triggers the intense metallic odor on the skin of hands used for food preparation. Biologists may interpret the distinctive and sensitive human smell for the (blood-)iron–skin odor as an evolutionary advantage that is much older than human use of metal tools: Early humans and their animal ancestors could probably like "blood-trailing" dogs track and locate wounded prey or tribal comrades by the metallic "blood scent" (of 1-octen-3-one etc.).

2) Pickled iron: carbon- and phosphorus-containing alloys of iron which are attacked by acid develop organophosphines with "garlic" metallic odor[4]

Human subjects also noted that even without skin contact a faint but different "garlic" metallic odor came from cast iron standard plates after contact with only artificial sweat or with 0.01N HCl. Phosphine (100 ng m^{-3} in the headspace gas (above the metal plate, under a glass funnel)) did not cause this odor. Complete dissolution of carbon- and phosphorus-rich iron filings in hot oxygen-free 1N HCl resulted in sufficiently concentrated gas for olfactometry and for identification and quantification of a variety of organophosphines by GC/MS and GC/ICP-MS (ICP = inductively coupled plasma; Table 1, and Supporting Information).

The "garlic" metallic odor (see Supporting Information) of the gas product from acidic dissolution of cast iron is dominated by these organophosphines. We measured an extremely low odor threshold for two key odorants, methylphosphine and dimethylphosphine (6 and 3 ng P/m^3, respectively, garlic-metallic odor), which belong therefore to the most potent odorants known. Phosphine (PH$_3$) is not important for this odor because we found it has a much higher odor detection threshold ($>10^6$ ng m^{-3}). A "calcium carbide" (or "burned lime"/"cement") attribute of the general "garlic" odor is probably caused by unsaturated hydrocarbons (alkynes, alkadienes) that are linked to a high carbon content of iron (Table 1, see Supporting Information).

It is clear that these organophosphines arise for the high carbon and phosphorus contents in iron (Table 1). The carbon and phosphorus are chemically reduced and alloyed with the iron metal (iron–magnetite redox buffer), and react with hydrogen on dissolution of the iron in acid (similar to phosphine[3] (PH$_3$) formation from reduced phosphorus-containing iron). Specifically, solid phases of iron phosphide (Fe$_3$P), iron carbide (Fe$_3$C, cementite), or Fe–C–P alloys, could form hydrocarbons and PH$_3$ on iron dissolution that partially combine in the early stages to form organophosphines.

Alternatively, the iron metal could already contain C–P bonds that survive iron dissolution, and acquire hydrogen, such as hypothetical "iron–carbon–phosphide" (-Fe-P-C-) or "iron–phosphorus–carbide" (-Fe-C-P-) bonds. However, that would prove present materials-science knowledge wrong in that phosphorus (a substitutional solid solute) and carbon (an interstitial solid solution) in iron do not bind for energetic reasons (see exception in ref. [12]).

To test this hypothesis we verified the presence of methylphosphinic acid (CH$_5$PO$_2$, up to 3 μg g^{-1}) in rusted cast iron samples that do not form PH$_3$ and hydrocarbons as intermediates in the oxidation (rusting) process. Methylphosphinic acid (also a metastable oxidation product of methylphosphine) can oxidize further to methylphosphonic acid,[13] has no biological source, and is placed on the Schedule list of the Chemical Weapons Convention (CWC, Schedule 2.B.4). These C–P compounds could also influence the corrosion of iron.[14]

In conclusion: 1) The typical "musty" metallic odor of iron metal touching skin (epidermis) is caused by volatile carbonyl compounds (aldehydes, ketones) produced through the reaction of skin peroxides with ferrous ions (Fe^{2+}) that are formed in the sweat-mediated corrosion of iron. Fe^{2+} ion containing metal surfaces, rust, drinking water, blood etc., but also copper and brass, give rise to a similar odor on contact with the skin. The human ability to detect this odor is probably a result of the evolutionarily developed but largely dormant ability to smell blood ("blood scent").

2) The "garlic-carbide" metallic odor of phosphorus- and carbon-rich cast iron and steel under attack by acid, is dominated by volatile organophosphines. Corroding cast iron is an environmental source of C–P compounds that may lead to confusion in the verification and monitoring of the Chemical Weapons Convention (see also ref. [15]).

Table 1: Production of volatile organophosphines and odors from dissolution of C–P-alloyed iron metal in hot oxygen-free HCl.

| Metal standard | Metal impurity μg element/g metal | | Odorants and odor from HCl dissolved metal | | | |
| | | | μg volatilized element/g metal | | | m^3 air/g metal dissolved |
	C	P	C as hydrocarbons[a]	P as PH$_3$	P as organophosphines[b]	Gas dilution to odor threshold[c]
Cast iron SCRM 665/3	32 100	11 100	1953	39	25	22 300
Cast iron SCRM 661/3	26 300	8300	5311	127	82	35 700
Cast iron SCRM 664/3	29 200	5500	3050	51	61	28 600
Cast iron SCRM 662/3	30 400	2500	5402	14	54	24 100
Cast iron SCRM 663/3	34 900	1030	4292	14	6	11 600
Steel CKD 165 H	1500	890	747	6	0.24	800
Steel CKD 162 H	200	50	216	0.27	0.01	26
Iron, ultra pure	<10	<1	<10	0.02	n.d.	n.d.
Aluminum 122/03[d]	<10	75	<10	35	n.d.	24
Aluminum 124/03[d]	<10	1	<10	0.54	n.d.	31

[a] Hydrocarbons include C$_1$–C$_6$ alkenes and alkynes. [b] Organophosphines (GC/MS, GC/ICP-MS) in the same gas samples comprise methylphosphine > dimethylphosphine > trimethylphosphine (or methylethylphosphine) ≫ ethylphosphine > propylphosphine. Other volatile odorants found are H$_2$S, alkylsulfides, AsH$_3$, methylarsine, dimethylarsine, formed from sulfur and arsenic impurities in the iron alloys. [c] Dilution-olfactometry data mean that the complete gas product (hydrogen with odorants) of just one gram of iron 661/3 dissolved in HCl can be diluted with 35 700 m^3 air before its odor becomes undetectable. One μg iron dissolved by the sweat of a human hand (instead of HCl) could explain a whiff of "garlic-carbide" metallic odor. The unit m^3 in the last column is akin to the odor unit (OU). [d] Aluminum is listed as a control (high PH$_3$, low odor). See Supporting Information.

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