Expanded Utility of the Beilstein Flame Test for Organically Bound Halogens as a Sensitive and Specific Flame Photometric Detector in the Gas Chromatographic Determination of R-X Compounds as Illustrated with Organochlorine Pesticides

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In 1962 we published (9) a brief note on the utility of the Beilstein flame test for organohalogen compounds as an adjunct (split stream) glc detector to signal their appearance in the emergent gas stream for facilitating their collection as organohalogen fractions for any purpose. We reported that about 0.17 μg. of organically bound chlorine/second was visually detectable with the conditions and apparatus used at that time. We further stated that enhanced minimum detectability could be achieved by filter

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photometry, spectrometry, and flame miniaturization. This progress report is to record further work in quantitative adaptations of this simple technique as a general purpose flame photometric detector for glc fractions containing organobromine, organochlorine, and organoiodine compounds at the nanogram and probably picogram level, with especial utility for applicable pesticide residue evaluations.

As we reported earlier (9), even applications of the 1872 Beilstein flame test as glc detectors are not new. The chronological history of these and the several simple "indicator" applications is summarized in Table 1. Both Beilstein (2) and Feigl (6) mentioned the superiority of CuO over clean Cu in the visual test. The first spectrographic application was in 1954 (15), the first adaptation to a microflame for enhanced minimum detectability was in 1955 (16), and the first applications to classical flame photometry were in 1957 (2) and 1958 (18); the first applications of this simple test as a glc detector apparently were in 1961 with both visual (4) and proposed photometric (5,22) "observation" of the Beilstein blue-green color. The first application to pesticide residue evaluations was in 1962 (9).

Several investigators have applied this detector and closely related flame emission detectors to the

Table 1--Chronological development of Beilstein flame photometric detection and determination of C-X

Author(s)	Year	Intended measurement qual.	Intended measurement quant.	Mechanism of introducing C-X	Detection (and measurement)	Application
Beilstein	1872	+	-	On CuO-coated Pt wire in flame	Visual	General for C-X
Hayman	1939	+	+[a]	In flame beneath red-hot monel metal tube	Visual	General for C-X
Ruigh	1939	+	+[a]	Vapor into flame beneath Cu gauze	Visual	General for C-X
Jurecek & Muzik	1950	+	-	In flame beneath Cu gauze	Visual	Specific for C-X
Honma & Smith	1954	+	+	Spectrographic	Photographic	Specific for C-X
Jurány	1955	+	+[a]	In flame issuing from Cu capillary tube	Visual	General for C-X
Honma	1955	+	+	$Cu(NO_3)_2$+aq. test solution aspirated into flame	Flame spectrometric[b]	For Cl^- in sea water
Feigl	1956[c]	+	+	In flame mixed with CuO	Visual	For C-X, CNO, CNS
Menis et al.	1957	+	+	$Cl^- + Ag^+ \rightarrow AgCl$; measured flame luminosity of excess Ag^+	Flame spectrometric[d]	For X^-
Anthers	1957	+	+[a]	Gas aspirated into flame bathing Cu disc	Visual	For X_2
Marsh	1958	+	+	See Honma above	Flame photometric[b]	For C-X
Maruyama & Seno	1959	+	+	$Cu(NO_3)_2$+C-X in DMF aspirated into flame	Flame spectrometric[b]	For C-X
Chovin et al.	1961	+	-	Glc effluent into flame onto Cu wire	Visual	For C-X
Monkman & Dubois; Dubois & Monkman	1961	+	+[a]	Glc effluent into flame with Cu helix	Photometric	For C-X
Gunther et al.	1962	+	+[a]	Glc effluent into flame through Cu gauze thimble	Visual & spectrometric	For C-Cl pest. residues
Gilbert	1966	+	+	Vapors into special burner to form InCl	Spectrometric[e]	For C-Cl
Gutsche et al.	1968a	+	+	See Menis et al. above	Spectrometric[f]	For Cl^- in milk
Gutsche & Hermann	1968	+	+	See Gutsche et al. above	Flame photometric[f]	For C-Cl pest. residues
Gutsche et al.	1968b	+	+	Vapor into special burner to form InCl	Spectrometric[e]	For C-Cl pest. residues
Nowak & Malmstadt	1968	+	+	Glc effluent into Na flame[g]	Flame photometric[h]	For C-X

a/ Suggested, some minimum detectabilities reported.
b/ CuCl emission band at 435.4 mμ.
c/ Also 1966 edition.
d/ Ag emission band at 328 mμ.
e/ InCl emission band at 359.9 mμ.
f/ Ag emission band at 338.3 mμ.
g/ Na flame enhanced by X^-.
h/ Na emission band at 589 mμ.

problem of detecting and measuring traces of halogens, halides, and organohalogen compounds (Table 1). These interesting variations include aspirating a copper salt into the flame (14,19), using the Ag emission band from excess Ag^+ in the reaction $Ag^+ + Cl^- \rightarrow AgCl$ (20), using in a special burner the very strong emission band of InCl rather than that of CuCl (8,12), and using the selective enhancement by halogens of one of the strong Na emission bands (23). Among these variations, the special-burner InCl modification (8) appears most promising for a variety of reasons (8,12) and may represent the most stable, sensitive, reproducible, and reliable flame photometric detector for monitoring glc effluents (manuscript in preparation) for organohalogen compounds.

In the meantime, our observations on the simply-constructed CuCl flame photometric detector may be of interest in stimulating immediate applications similar to those already so broadly achieved with the well known glc flame photometric detectors for P- and S-containing organic compounds. Clearly, interchangeable specific-element detectors offer many advantages, but the possibility of grouping these 3 detectors into a single unit with a single flame is remote because of the widely different gas-flow ratios required by the present system; however, P and S flame photometric detectors are not so sensitive to gas flow and these photometric detectors have already been paired (3).

Luminescent flames bearing organic compounds (including solvents) show complex carbon emission bands, with major emissions at 305.4 (?), 307.7 (CO?), 311.0 (CHO?), and 421.0 (CO^+?) mμ; this last band becomes a doublet (423 mμ, also) when Cu is also in the flame. Ag^+, as used by Menis et al. (20), has strong emission at 328 mμ; this band may actually be due to AgCl (strong system from 311.4 - 337.9 mμ) or to AgH (327.5 mμ) in the H_2-O_2 flame utilized; Ag_2, AgBr, AgCl, AgI, and AgH have complex emission "spectra" (24). Similarly, the spectrum attributed to InCl in an H_2-air flame is complex, with 12 good maxima between 335 and 380 mμ, but with very intense emission at 359.9 mμ (8). On the other hand, the CuCl spectrum in an H_2-air or H_2-O_2 flame has at least 20 reasonable maxima between about 320 and about 520 mμ (19,24); several of these maxima are nearly 10 mμ in base width with numerous shoulders. Sharp bands at 323.2 and 334.4 mμ are Cu emission bands, but four very sharp and intense CuCl band heads occur at 418.8, 425.8, 428.0, and at 435.4 mμ (corrected). CuO bands appear between 491.7 and 453.2 mμ and at 523.7 mμ. Strong Na bands appear between 504 and 481 mμ and in the ultraviolet region. Whether the present Beilstein flame is actually due to CuCl or to Cu, CuH, CuO, and

CuOH may be controversial (e.g., see ref. 8), but Cl in the flame is required to produce the strong 418.8 and 435.4 bands.

It is thus clear that a good monochromator with wide slit is required for maximum reliability, sensitivity, and specificity in the present applications (Table 1). However, a 5- or 10-mμ band pass filter peaking at about 419, 427, or 435 mμ will provide adequate resolution and minimum detectability for many purposes. We have evaluated both Cu salt and metallic Cu emission-detection systems with a Beckman DK-2 recording spectrophotometer with aspirating-type flame photometric attachments, a Jarrell-Ash 0.5 meter Ebert spectrometer model 82-000 equipped with an EMI photomultiplier tube No. 6256B, and a Micro-Tek flame photometric detection system with a 1-inch o.d. 440-mμ monochromatic transmission filter (band width about 420 mμ to about 450 mμ, Photovolt Corporation).

Minimum detectability for chloride is very poor with Cu^{++} aspirated into an H_2-O_2 macroflame; for example, 1062 p.p.m. of Cl (from dieldrin) in 1270 p.p.m. of Cu^{++}, both in DMF, gave a good response at 435.4 mμ, whereas half this amount of Cl gave no response over background from 400-450 mμ at optimum settings with the flame photometric attachment for the DK-2 spectrophotometer. Further, there was also no response from 635 p.p.m. of Cu^{++} and 710 p.p.m. of Cl with this macroflame.

Inserting CuO-coated Cu wire 2 or 3 mm. into the base of a microflame in the manner of Chovin et al. (4) (see Table 1) did not provide quantitative responses, for much of the aspirated Cl by-passed the wire "pinnacle." The insertion of the Cu in the form of a loose coil the diameter (ca. 4 mm.) of the flame but half its height (ca. 20 mm.) into the lower portion of the flame issuing from a 1-mm. i.d. quartz capillary was reproducibly stable and sensitive to μg. quantities of Cl at the wide slit widths (up to 2.0 mm.) possible with the DK-2; with the narrow slit (400 μ maximum) of the Jarrell-Ash adequate optical alignment of the back-up concave mirror, the flame, and the monochromator presented a day-to-day problem for good reproducibility of minimum detectable amounts of Cl. With an H_2-O_2 flame the CuO and Cu are short-lived, but a 1:1:1 mixture of H_2:O_2:N_2 is not appreciably corrosive to this coil; presumably the minimum H_2 to maintain the flame at the lowest possible temperature that would maintain oxidizing conditions in the outer cone would be optimum. Alternatively, the tip of the microburner can consist of a 1-mm. hole drilled through a tight pellet of CuO granules, as with the CsBr "pellet" version of one of the so-called thermionic glc detectors for P. In either of these versions of the Cl detector, the compound of interest may be introduced into the burner via either the H_2 or the N_2 stream.

Various methods of introducing Cu(CuO) into the emission flame of the Micro-Tek flame photometric detector system containing a 440 mμ filter were used: 12-, 20-, and 32-gauge pure Cu wire were evaluated as "pinnacles" in the center of this multiflame burner, as doughnuts projecting into the flame cavity, as loose coils of various diameters projecting above the flame cavity, and as flat spirals placed across the top of the microburner hex-nut flame shield. A 3/8" o.d. loose flat spiral formed from 3" of the 32-gauge wire was the most satisfactory source of Cu atoms (ions) in terms of reproducibility and minimum detectability.

The response of this system is strikingly dependent upon oxygen concentration, since an oxidizing flame is essential with Cu wire; the optimum gas mixture approximates O_2 = 39 cc./min., H_2 = 78 cc./min., and N_2 = 80 cc./min. Reproducibility of this system will depend largely upon the stability of the flow control of these 3 gases. For example, 3 μg. of aldrin (58.3% Cl) in hexane (1 μg./μl.) gave the following responses (Aerograph 1520B; 10% DC-200 on 80/100 mesh Gas-Chrom Q in a 4' x 1/4" stainless steel column; injector 300°C.; column 205°C.; detector 185°C.):

Gas flow (cc./min.)			Recorder response
O_2	H_2	N_2	(units)
20	100	80	1.5
37	78	80	66
39	78	80	160 (attenuated to same scale)
ca. 41	78	80	*ca.* 3

With the column and other parameters specified above, detector response was reproducible but non-linear, as would be expected if Cu atoms (ions?) and Cl atoms (ions?) paired in the corona of the flame and also if Cl atoms (ions?) stripped Cu atoms (ions?) from the CuO-coated wire. An arithmetic plot of μg. of aldrin injected vs. recorder response exhibited a gentle "S" shape over the range 1 to 5 μg. at an O_2 flow rate chosen so that 2.5 μg. of aldrin gave 50 units pen response on a 90-unit scale. Responses were as follows (aldrin retention time 4 min.):

Aldrin (μg.)	Recorder response (units)
1.1	12.0 ± 0.7
2.0	31.5 ± 1.0
3.0	67.0 ± 1.6
4.0	78.0 ± 2.1
4.5	82.5 ± 2.5

Reproducibility at optimum O_2 flow rate was poorer since our gas flow regulators possessed an inherent ± 1% flow variation. All aldrin peaks had a peak width at half-height of 0.15 ± 0.02 inch at a chart speed of 0.5"/min.

At optimum O_2 flow rate (ca. 39 cc./min.), 20 ng. of aldrin was demonstrably detectable over the baseline noise of 0.5 chart unit. It is thus clear that this detector, with proper engineering and precision gas-flow regulation, is capable of far greater minimum detectability and reproducibility. If ions rather than atoms or free radicals are involved in the chemistry of this CuCl emission detector, about a 90-volt D.C. potential impressed across burner and Cu source should markedly increase the efficiency of response.

After 40 injections, the Cu spiral had a clean Cu center and CuO-coated outer edges; there was no significant corrosion of the 32-gauge wire. Doubling the length of Cu wire in the spiral markedly decreased detector response, so there is an optimum amount of Cu surface for the flame flow pattern of the present burner.

Feigl (6) claims C-X compounds yield HX upon ignition, and CuO (not Cu)+HX→CuX+CuX_2 (6,25), and that CuX or CuX_2 supply the emission bands of interest in a non-luminous flame; Honma (14) first provided strong evidence to support the major contribution by CuX. $COCl_2$ may also be produced (25). Certain N-containing compounds also contribute to this test (6), possibly through the pyrolytic release of NH_3, HCN, or HNC (6,21,27) and should be compensated if present in the sample under examination; Jurecek and Muzik (17) claim that any substance yielding volatile Cu compounds under flame pyrolytic conditions may give positive responses in the Beilstein test. Factors affecting emission intensities in flame photometry have been reviewed by Foster and Hume (7).

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