Electronic Supplementary Material

Reduced texaphyrin: A ratiometric optical sensor for heavy metals in aqueous solution

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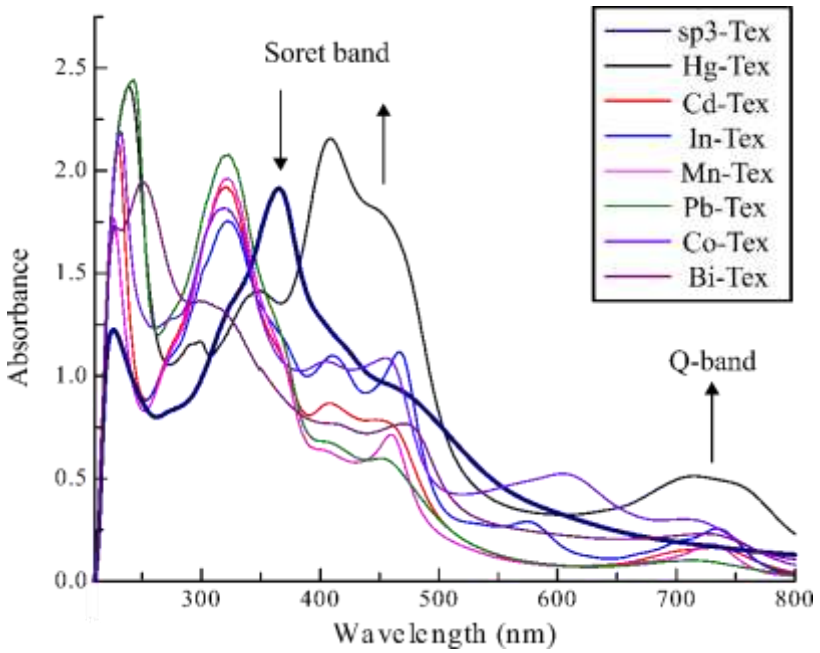

Figure S1. UV-Vis absorption spectra of solutions resulting from mixing sp3-Tex (ligand **1**; 0.1 mM in aqueous acetate buffer) with metal salts (1 mM in 1:1 acetic acid:acetate aqueous buffer solution) and heating for 10 minutes. All samples containing these cations were characterized by a shift in the Soret band from 365 nm to 467 nm as well as an emerging Q-type band at 735 nm.

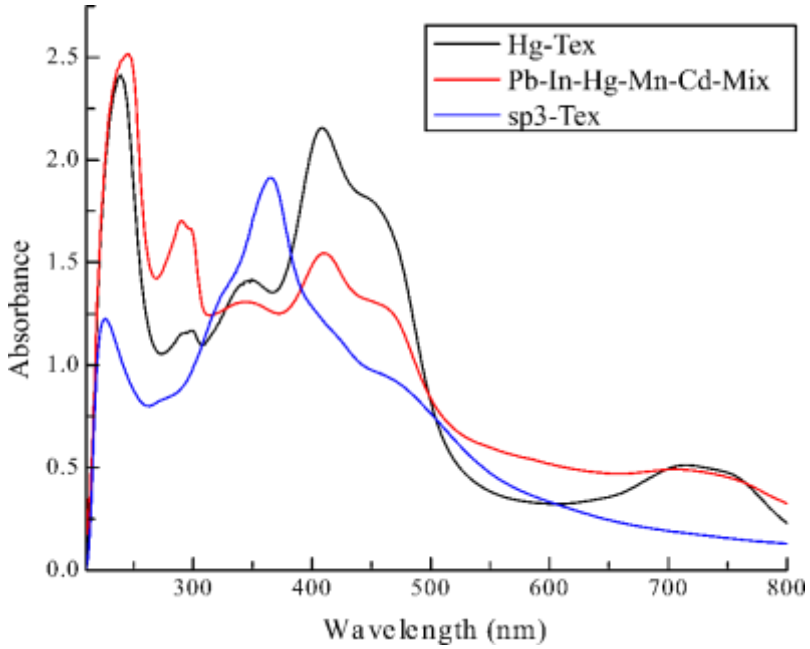

Figure S2. UV-Vis absorption spectra of the solutions produced by mixing $Hg(OAc)_2$ with **1** in aqueous acetate buffer (black line), the indicated mixture of metal cations (red line), and unreacted ligand (sp3-Tex, **1**). That the same line shape was seen for both metalation studies was taken as initial evidence that only the Hg(II) complex is formed in a mixture of the indicated metal salts.

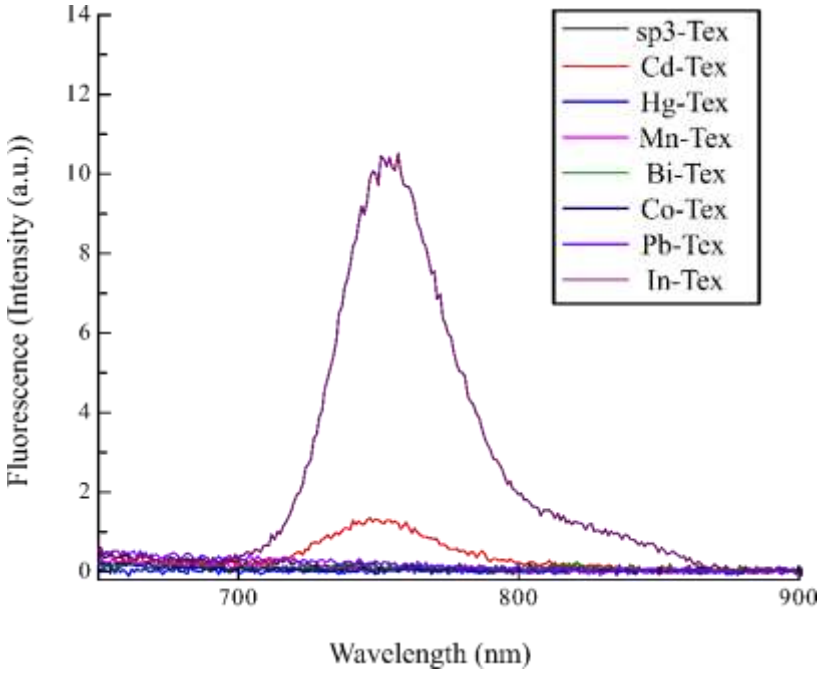

Figure S3. Fluorescence spectra of each suspected metal complex (0.1 mM solutions in aqueous acetate buffer at pH ≈ 5-6, λ_{ex} = 740 nm, λ_{max} = 752 nm). The only two metal ions to produce a discernible fluorescent signal were Cd(II) and In(III). In the case of In(III) the fluorescence increase produced a signature that could be seen by the naked eye under conditions of illumination with a handheld UV lamp. See main text.

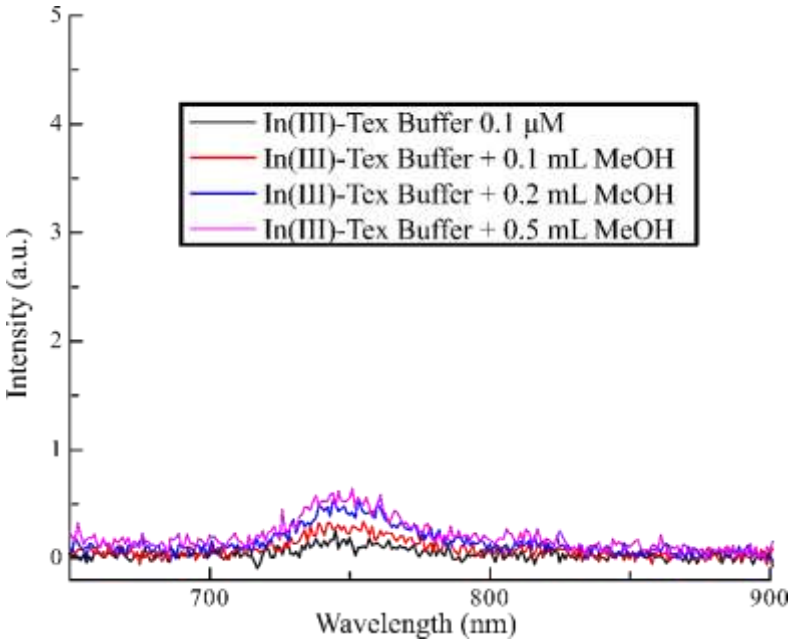

Figure S4. Fluorescence spectra recorded as methanol was added to In(III)-Tex in water. The increase in fluorescence is thought to be due to the disaggregation of texaphyrin species typically seen in more hydrophobic media.

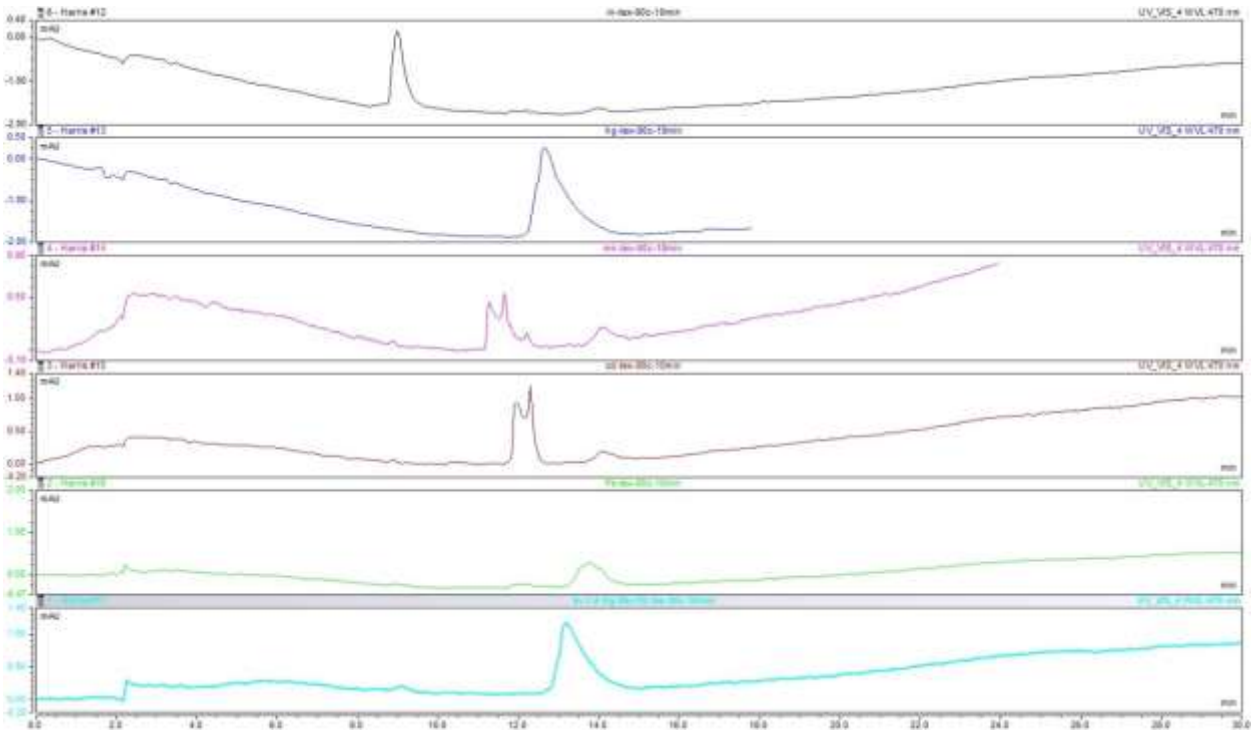

Figure S5. HPLC traces of the solutions resulting from mixing **1** (0.1 mM in aqueous acetate buffer) with $InCl_3$, $Hg(OAc)_2$, $Mn(OAc)_2$, $Cd(NO_3)_3$, and $Pb(NO_3)_2$ (1 mM in 1:1 acetic acid:acetate aqueous buffer solution) and heating for 10 minutes. All traces show a peak at a retention time between 9-14 minutes, values that are typical for texaphyrin complexes under conditions of HPLC analysis ($\lambda_{detector}$ = 470 nm, Syncronis C18 column, 5 μm, 4.6 x 250 mm (Thermo Scientific); the mobile phase consisted of an increasing gradient (from 10% to 99% in 10 min) of

acetonitrile in water, both containing 0.1% acetic acid. Flow rate was set to 1.2 mL / min). A test involving a mixture of metal cations produces only one peak with in the chromatogram. This peak has the same retention time as Hg(II)-Tex. This was taken as further evidence of preferential Hg(II) complexation. See main text for discussion.

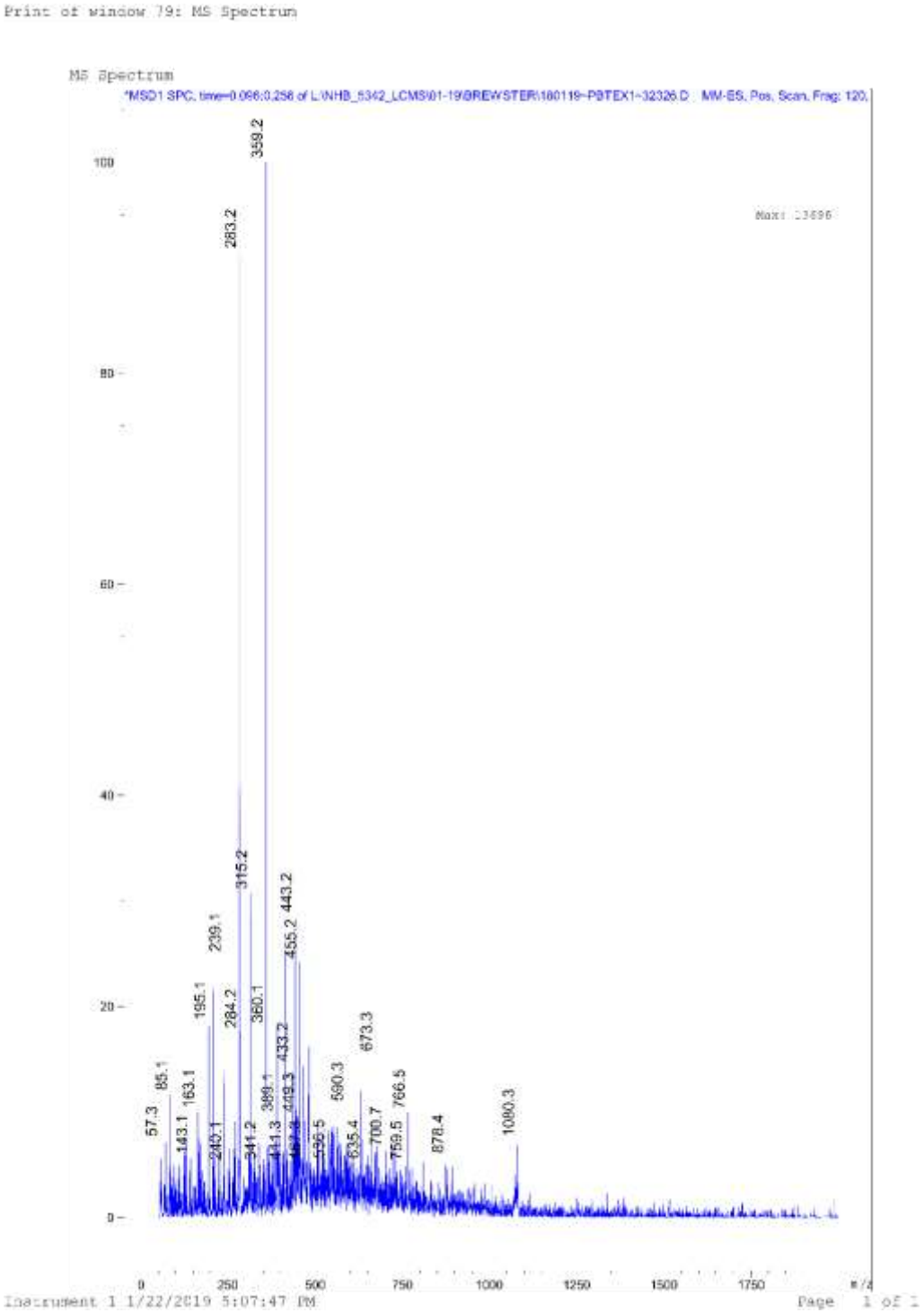

Figure S6. Low-resolution mass spectrum of the crude mixture obtained by mixing $Pb(NO_3)_2$ with **1** in an aqueous acetate buffer. The peak at 1080.3 corresponds to the M^+ of Pb-Tex.

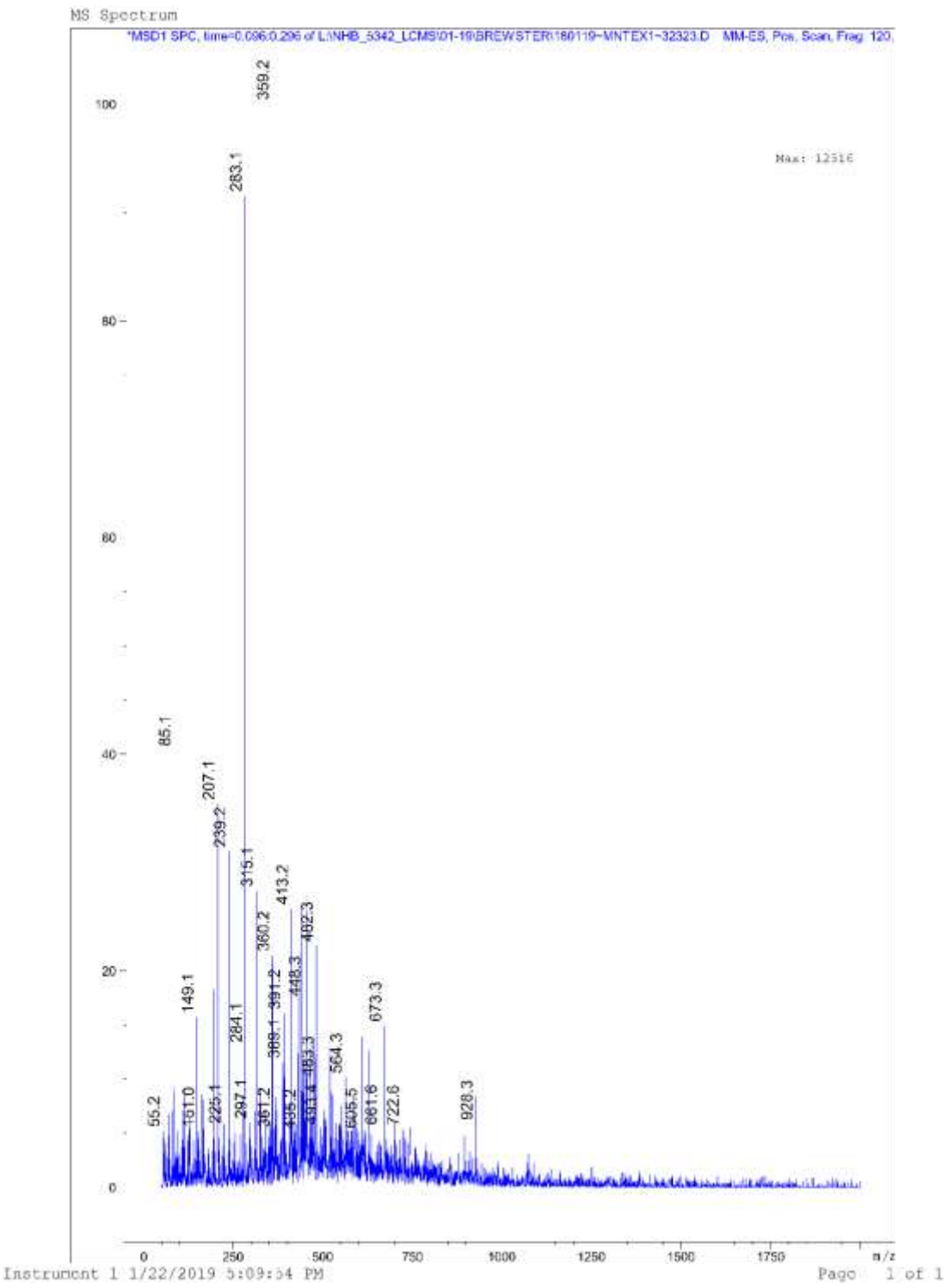

Figure S7. Low-resolution mass spectrum of the crude mixture obtained by mixing $Mn(OAc)_2$ with **1** in an aqueous acetate buffer. The peak at 928.3 corresponds to the M^+ of Mn-Tex.

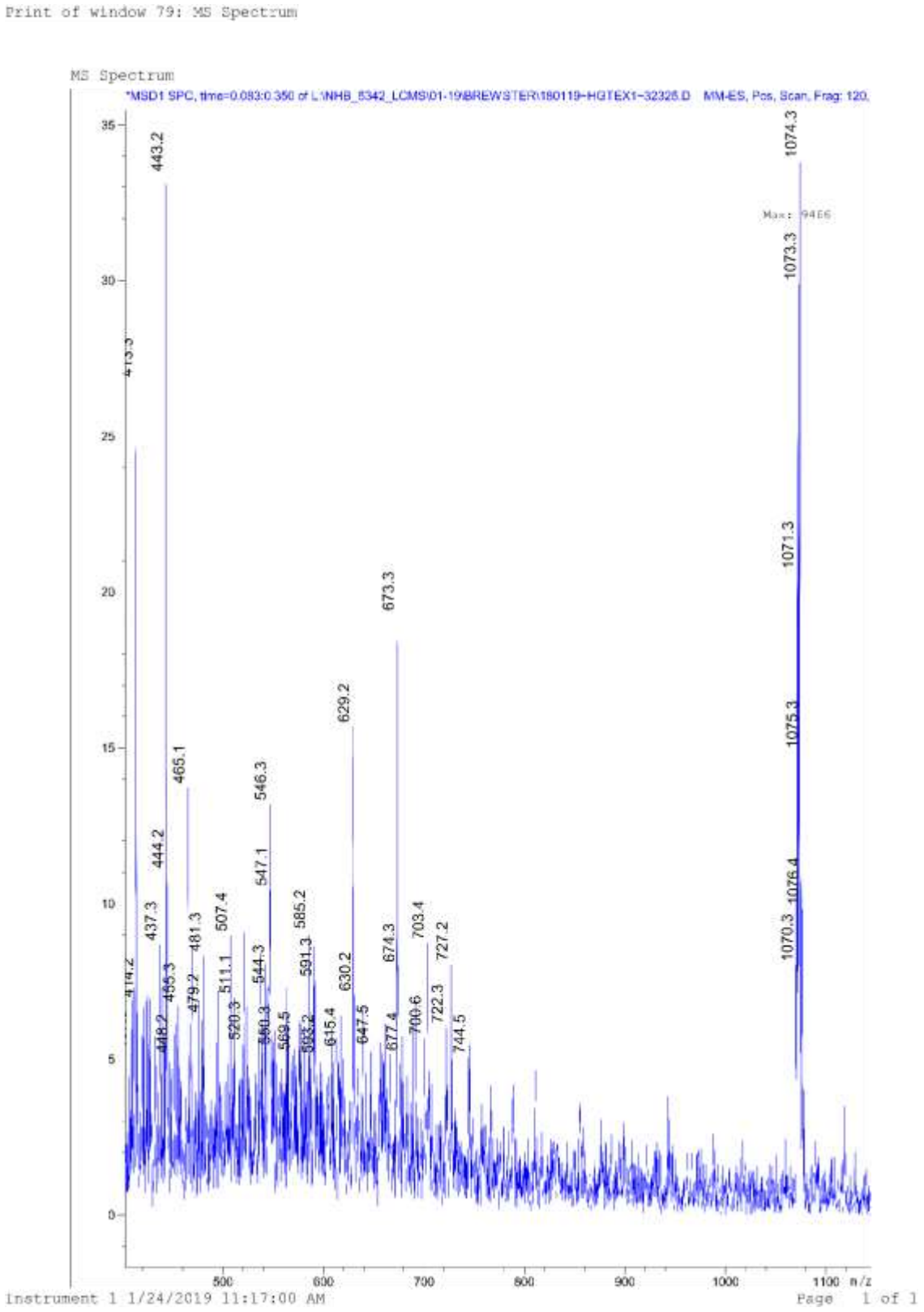

Figure S8. Low-resolution mass spectrum of the crude mixture obtained by mixing $Hg(OAc)_2$ with **1** in an aqueous acetate buffer. The peak at 1074.4 corresponds to the M^+ of Hg-Tex.

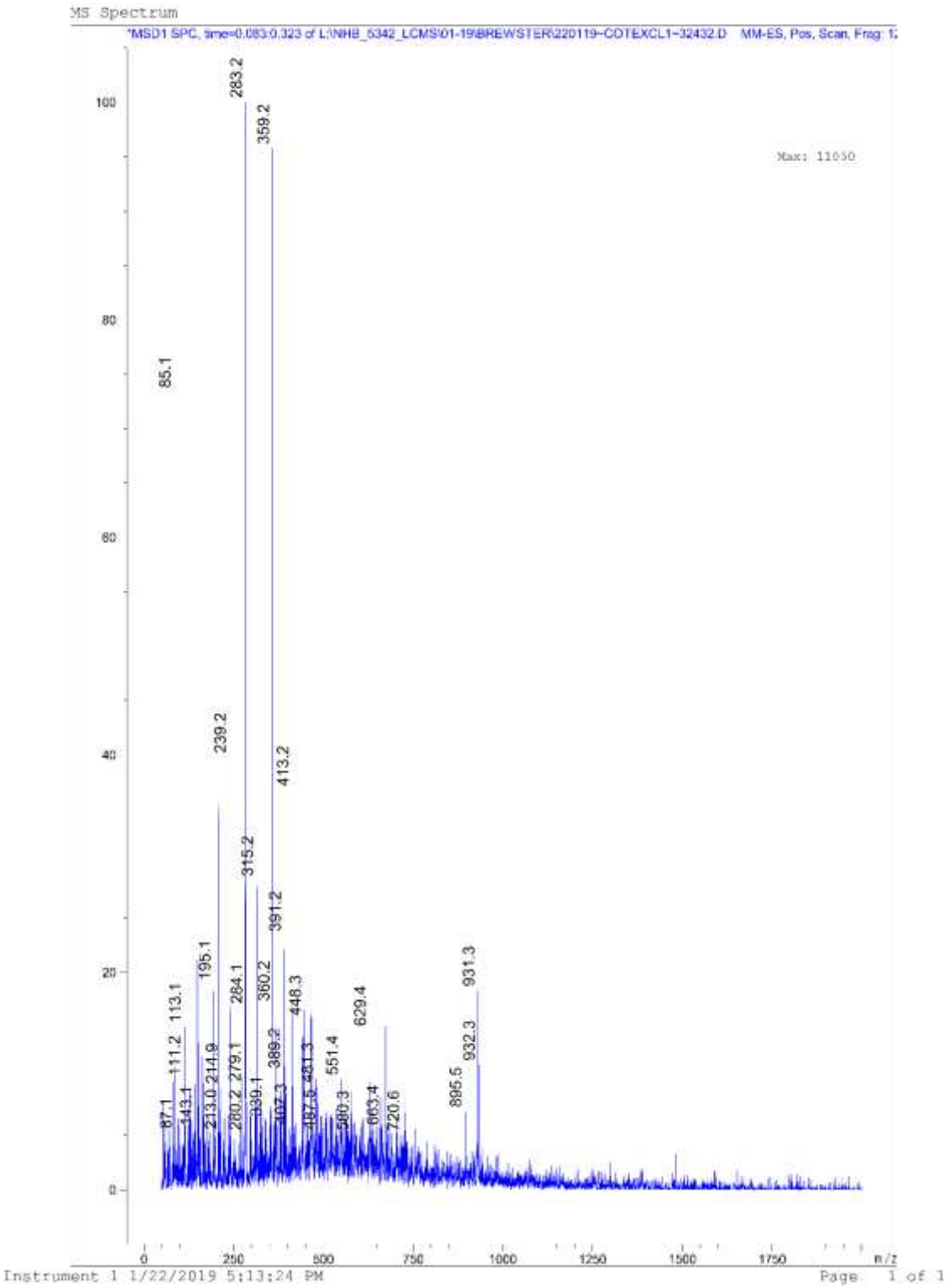

Figure S9. Low-resolution mass spectrum of the crude mixture obtained by mixing $Co(NO_3)_3$ with **1** in an aqueous acetate buffer. The peak at 931.3 corresponds to the M^+ of Co-Tex.

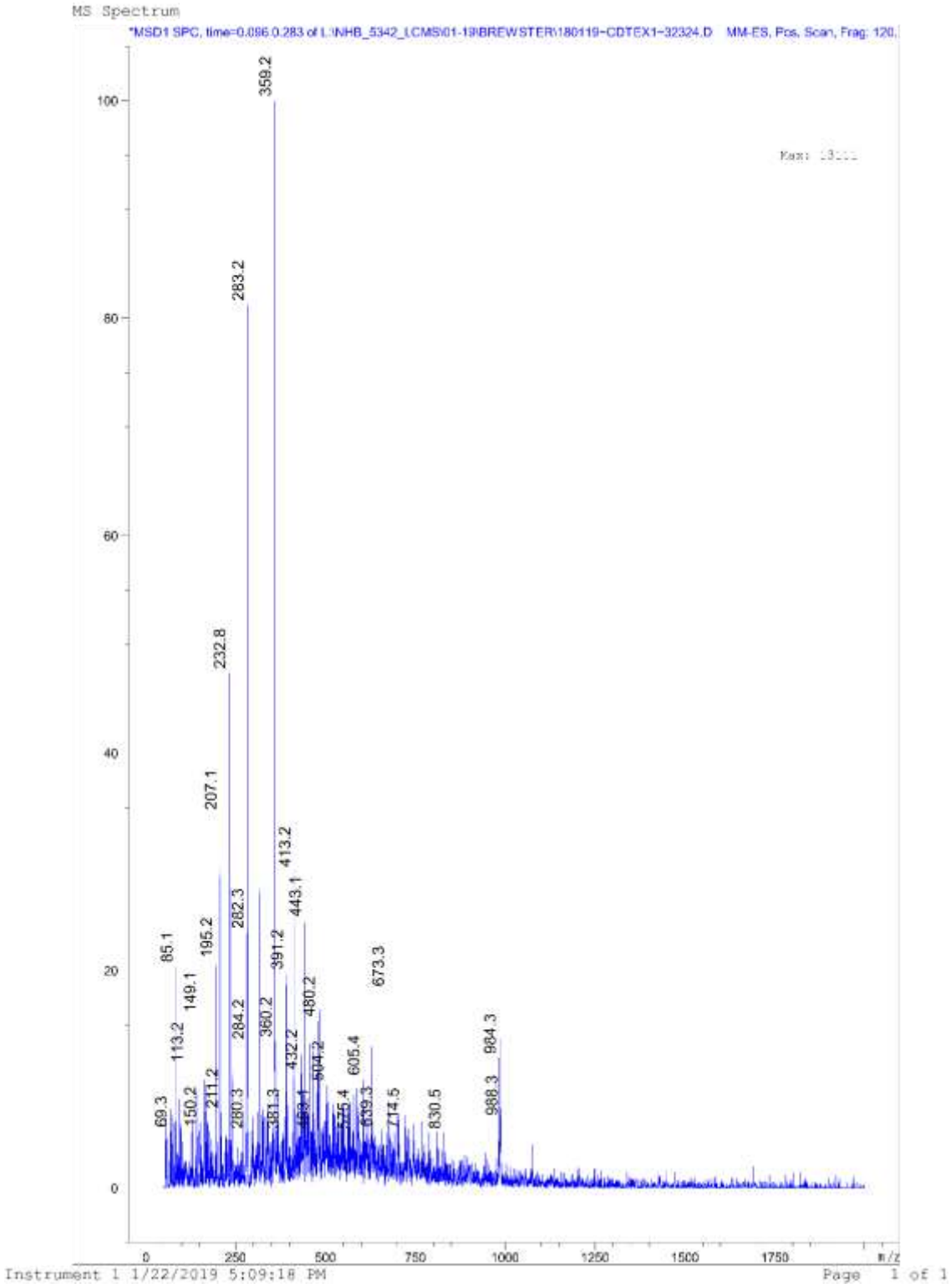

Figure S10. Low-resolution mass spectrum of the crude mixture obtained by mixing $Cd(NO_3)_3$ with **1** in an aqueous acetate buffer. The peak at 986.3 corresponds to the M^+ of Cd-Tex.

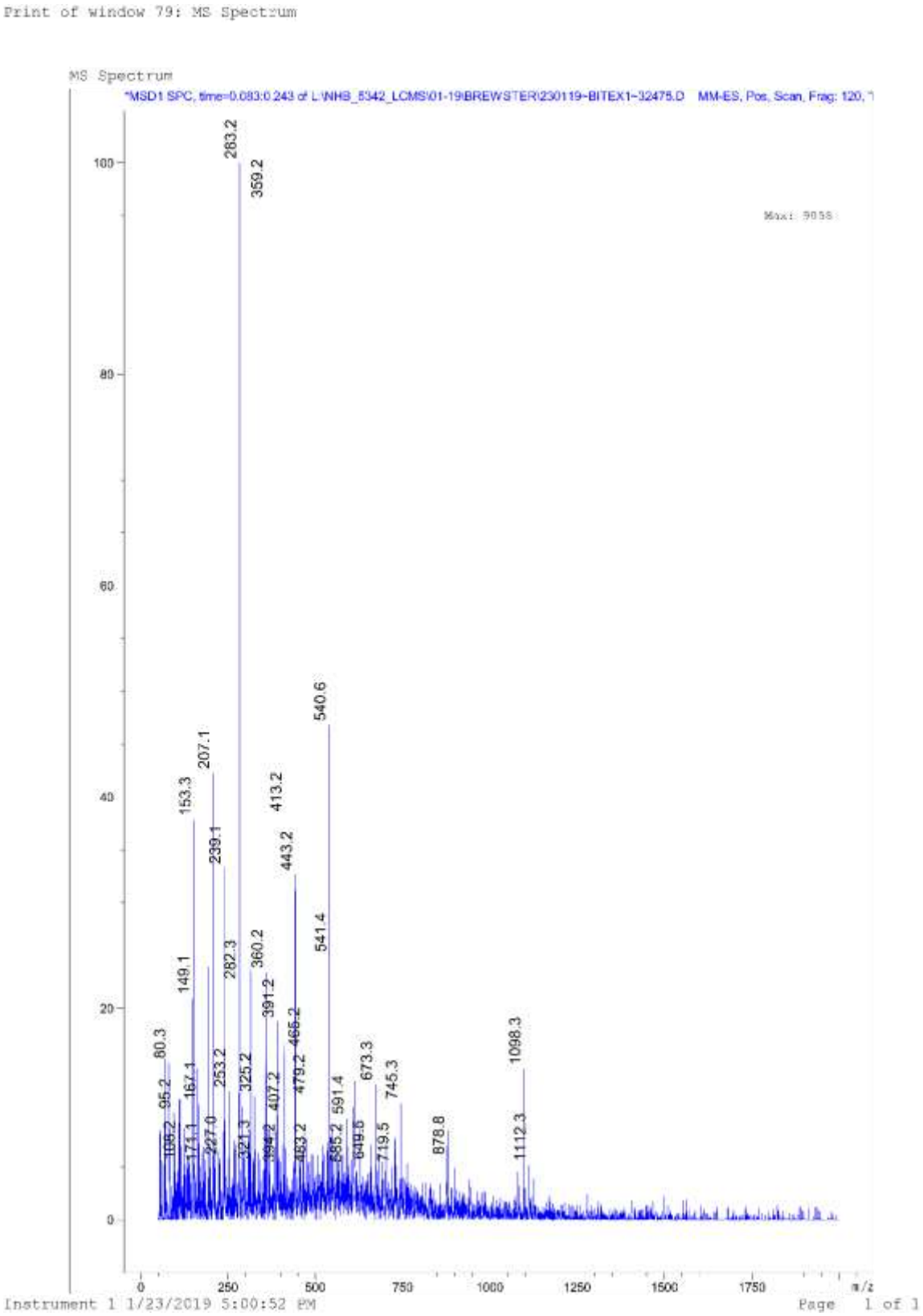

Figure S11. Low-resolution mass spectrum of the crude mixture obtained by mixing $Bi(OAc)_3$ with **1** in an aqueous acetate buffer. The peak at 1098.3 corresponds to the M^+ + OH of Bi-Tex.

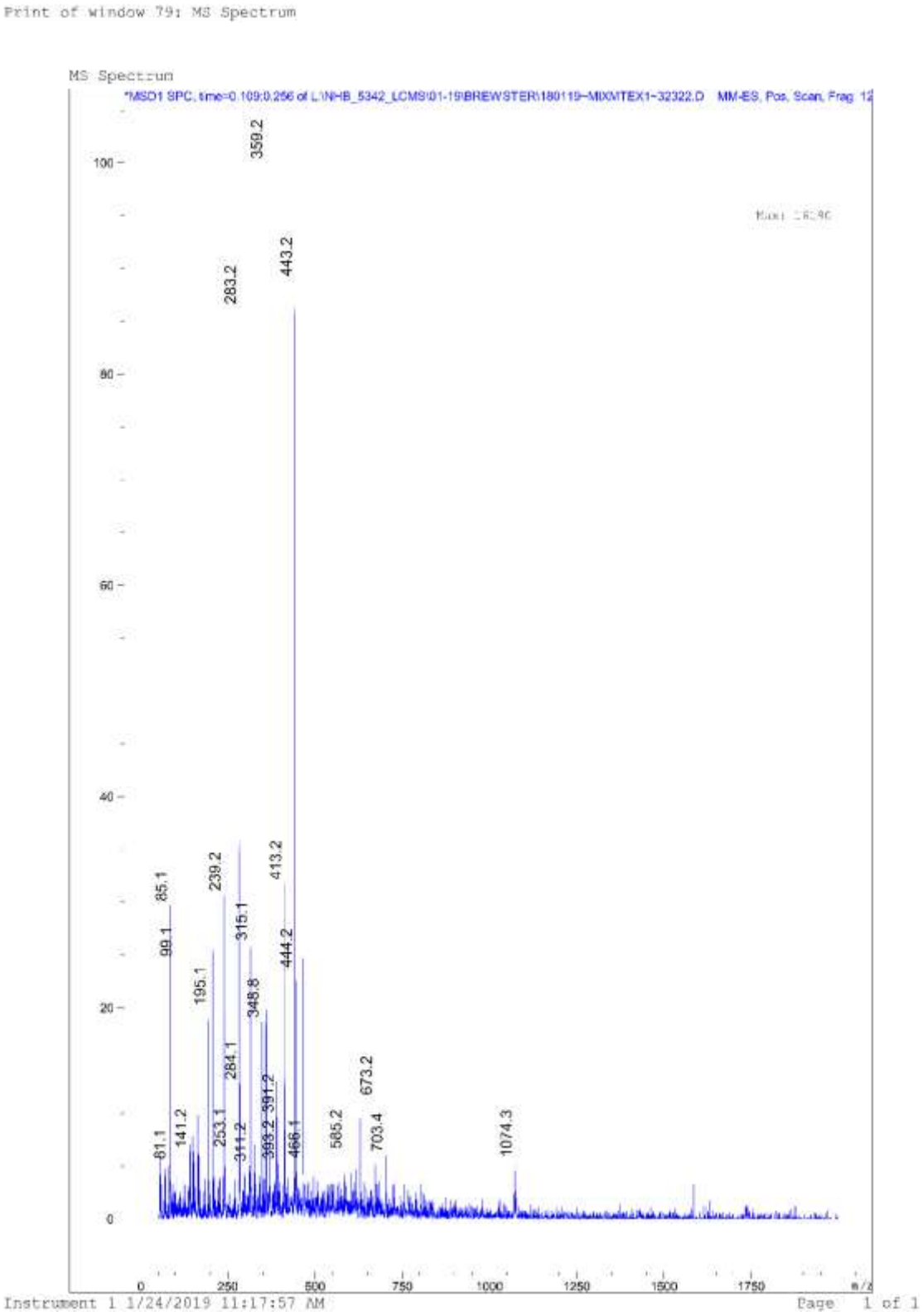

Figure S12. Low-resolution mass spectrum of the crude mixture obtained by mixing $InCl_3$, $Hg(OAc)_2$, $Mn(OAc)_2$, $Cd(NO_3)_3$, and $Pb(NO_3)_2$ with **1** in an aqueous acetate buffer. The peak at 1074.3 corresponds to the M^+ of Hg-Tex,no other metal complexes are observed.

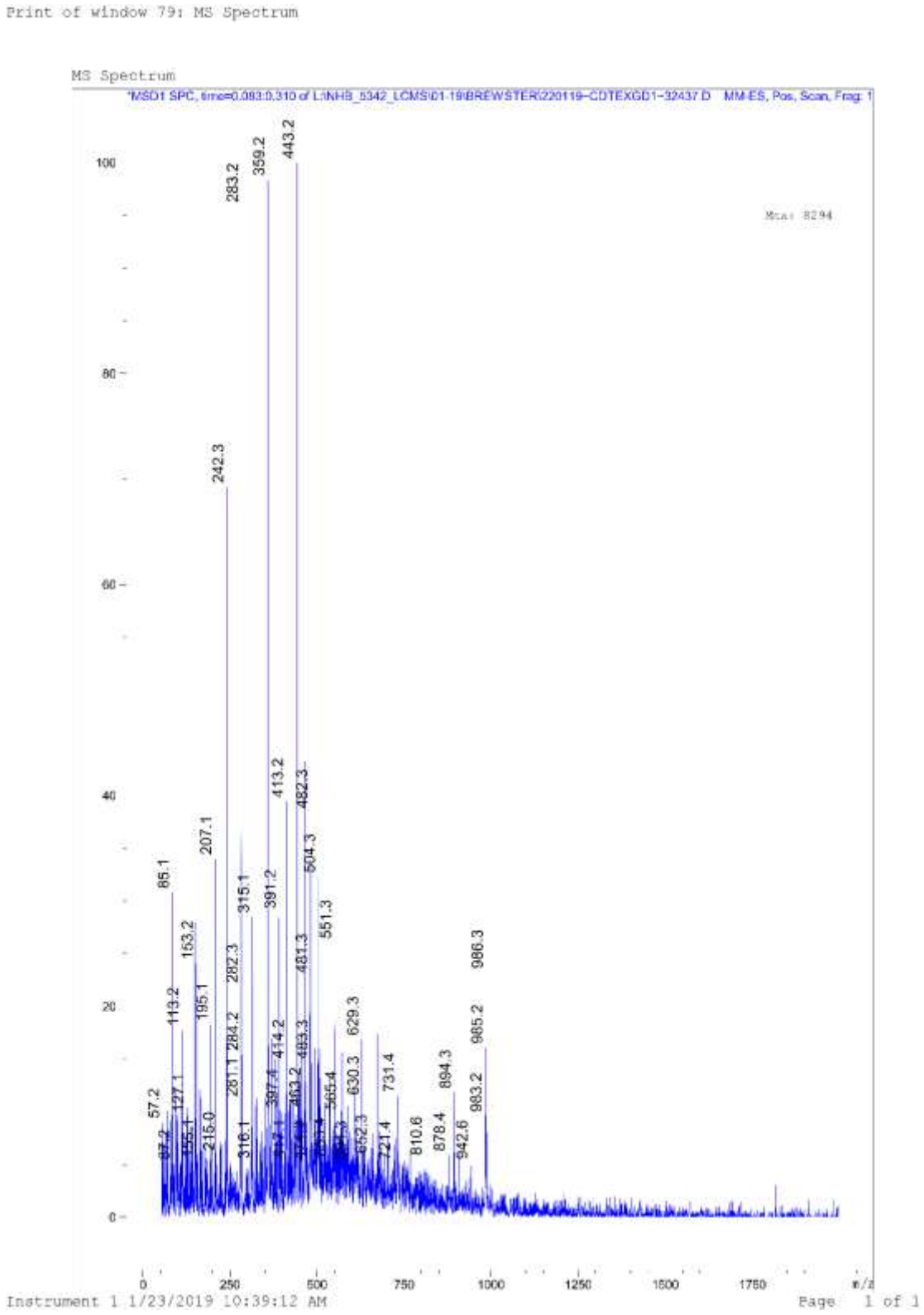

Figure S13. Low-resolution mass spectrum of the crude mixture obtained by mixing $Gd(OAc)_3$ with preformed Cd-Tex in an aqueous acetate buffer. The peak at 986.3 corresponds to the M^+ of Cd-Tex, Gd-Tex is not observed.

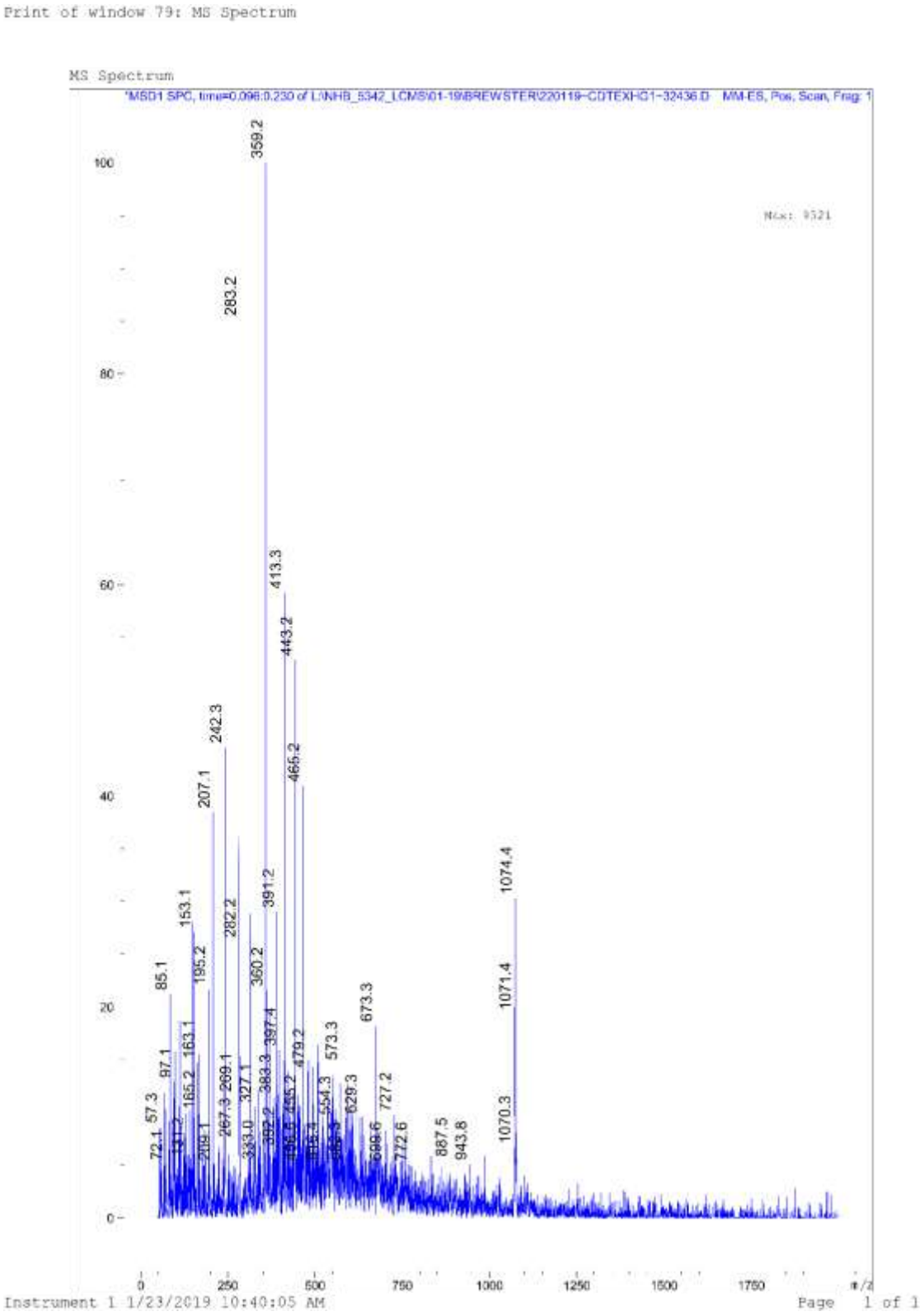

Figure S14. Low-resolution mass spectrum of the crude mixture obtained by mixing $Hg(OAc)_2$ with preformed Cd-Tex in an aqueous acetate buffer. The peak at 1074.4 corresponds to the M^+ of Hg-Tex, Cd-Tex is not observed.