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A simple, non-chromatographic and green method based on flow injection UV photochemical and ultrasonic vapor generation atomic fluorescence spectrometry has been developed for the determination and speciation analysis of mercury. Mercury cold vapor (Hg⁰) was obtained only using formic acid and UV or ultrasonic irradiation by this method, and was subsequently detected by AFS. Both mercury (Hg²⁺) and methyl mercury (MeHg) can be converted to Hg⁰ for the determination of total mercury with UV irradiation; while only Hg²⁺ can be reduced to Hg⁰ with the ultrasonic irradiation, thus determining Hg²⁺ only. Then, the concentration of MeHg can be calculated by subtracting the Hg²⁺ concentration from the total mercury concentration. The optimal conditions for the best cold vapor generation efficiencies are discussed in detail, together with the interference from transition metals. This new speciation method not only provides high sensitivity for determination of mercury species but further eliminates use of toxic or expensive reducing reagents, minimizes the contamination sources and avoids potential destruction of analyte species occurred in chromatographic separation methods. Moreover, a simpler and less toxic Hg2+ standard series can be used for the calibration of both Hg^{2+} and MeHg. The limit of detection is 0.005 or 0.01 mg L⁻¹ for total mercury with the UV or inorganic mercury with the ultrasonic irradiation, respectively. The accuracy of this method was validated by determination of mercury in river water, tap water and certified reference material (Tuna fish).