The procedure recommended by radiation dosimetry protocols for determining the collection efficiency f of an ionization chamber assumes the predominance of general recombination and ignores other charge loss mechanisms such as initial recombination and ion diffusion. For continuous radiation beams, general recombination theory predicts that f can be determined from a linear relationship between $1/Q$ and $1/V^2$ in the near saturation region $(f > 0.7)$, where Q is the measured charge and V the applied chamber potential. Measurements with Farmer-type cylindrical ionization chambers exposed to cobalt-60 gamma rays reveal that the assumed linear relationship between $1/Q$ and $1/V^2$ breaks down in the extreme near-saturation region $(f > 0.99)$ where Q increases with V at a rate exceeding the predictions of general recombination theory.

We have developed a comprehensive model to describe the saturation characteristics of ionization chambers. The model accounts for dosimetric charge loss (initial recombination, ion diffusion, and general recombination) and non-dosimetric charge multiplication in an ionization chamber, and suggests that charge multiplication plays a significant role under typical chamber operating conditions (300 V) used in radiation dosimetry. Through exclusion of charge multiplication from the measured chamber signal Q, the model predicts the breakdown of the $1/Q$ and $1/V^2$ relationship and shows that the final approach to saturation is governed by initial recombination and ion diffusion which are characterized by a linear relationship between $1/Q$ and $1/V$. Collection efficiencies calculated with this model differ by up to 0.4% from those determined through a rigorous application of general recombination theory alone.