Supporting Information

Following treatment will show that the pK_a values could be used to calculate the concentration of the free base.

$$PhNH_2 + HOAc = PhNH_3^+ + OAc^- \qquad K$$

$$K = [PhNH_3^+][OAc^-]/[PhNH_2][HOAc]$$

$$HOAc + H_2O = H_3O^+ + OAc^- \qquad K_{a1}$$

$$K_{a1} = [H_3O^+][OAc^-]/[HOAc][H_2O]$$

$$PhNH_3^+ + H_2O = PhNH_2 + H_3O^+ \qquad K_{a2}$$

$$K_{a2} = [H_3O^+][PhNH_2]/[PhNH_3^+][H_2O]$$

$$K = K_{a1}/K_{a2} = ([H_3O^+][OAc^-]/[HOAc][H_2O])/([H_3O^+][PhNH_2]/[PhNH_3^+][H_2O])$$

In absence of water there is no self ionization of HOAc and hence $[PhNH_3^+] = [OAc^-]$

$$[PhNH_3^+] = ([PhNH_2]_T - [PhNH_2])$$

$$\text{Hence } K_{a1}/K_{a2} = ([PhNH_2]_T - [PhNH_2])^2/[HOAc][PhNH_2]$$

$$(K_{a1}/K_{a2})[HOAc][PhNH_2] = [PhNH_2]_T^2 - 2[PhNH_2]_T[PhNH_2] + [PhNH_2]^2$$

$$[PhNH_2]^2 - \{K_{a1}[HOAc]/K_{a2}) + 2[PhNH_2]_T\}[PhNH_2] + [PhNH_2]_T^2 = 0$$

$$x^2 - bx + c = 0$$

$$x = [PhNH_2];\ b = \{(K_{a1}[HOAc]/K_{a2}) + 2[PhNH_2]_T\};\ c = [PhNH_2]_T^2$$

$$x = [b \pm \sqrt{(b^2 - 4c)}]/2$$

Since K_{a1}, K_{a2} and $[PhNH_2]_{Total}$ are known and [HOAc] is determined experimentally $[PhNH_2]$ is calculated; a computer program (C++) could be used.

pK_a values: Acetic acid: 4.76; Aniline: 4.60; *m*-methylaniline: 4.71; *m*-aminophenol: 4.31; *m*-chloroaniline: 3.52; *m*-nitroaniline: 2.46; *m*-aminobenzoic acid: 3.07; *m, p*-dimethylaniline: 5.17; *m, p*-dichloroaniline: 2.96; *p*-methylaniline: 5.08; *p*-methoxyaniline: 5.36; *p*-ethoxyaniline: 5.25; *p*-chloroaniline: 3.99; *p*-bromoaniline: 3.88; *p*-nitroaniline: 1.01; *p*-aminobenzoic acid: 2.41; ethyl *p*-aminobenzoate: 3.33; *p*-aminoacetanilide: 4.60; *o, m*-

dichloroaniline: 1.76; *o*-methylaniline: 4.45; *o*-methoxyaniline: 4.53; *o*-ethoxyaniline: 4.47; *o*-chloroaniline: 2.64; *o*-nitroaniline: -0.28; *o*-aminobenzoic acid: 2.09; methyl *o*-aminobenzoate: 2.36; *o*-aminoacetophenone: 2.22; *o*-phenylenediamine: 4.65 (1.86); N-methylaniline: 4.85; N,N-dimethylaniline: 5.15; the value given in parenthesis corresponds to $pK_{a(2)}$.