Yes, I think it is possible that a sitter not dealing with a companion sitting placement service could be a household employee of the recipient of services. We would apply the common law factors to determine whether the relationship of employer-employee exists. This is reflected in example 3 of the regulations at section 31.3506-1(e):

Example (3). As a service to the community, a neighborhood association maintains a list of individuals who are available to babysit. Parents in need of a sitter contact the association and are provided with a list of names and telephone numbers. The association charges no fee for the service and takes no action other than compiling the list of sitters and making it available to members of the community. Issues such as hours of work, amount of payment, and the method by which the services are performed are all resolved between the sitter and parent. A, a parent, used the list to hire B to sit for A’s child. B performs the services four days a week in A’s home and follows specific instructions given by A. Under § 31.3121(d)-1, B is the employee of A rather than the employee of the neighborhood association. Consequently, this section does not apply and B remains the employee of A.

I have not reviewed the training materials in their entirety (so I hesitate to suggest changes), but if you wanted to make this point in the paragraph below, here is a suggestion (in bold):

Companion sitters are individuals who furnish personal attendance, companionship, or household care services to children or to individuals who are elderly or disabled. A person engaged in the trade or business of putting the sitters in touch with individuals who wish to employ them (that is, a companion sitting placement service) will not be treated as the employer of the sitters if that person does not receive or pay the salary or wages of the sitters and is compensated by the sitters or the persons who employ them on a fee basis. Companion sitters who are not employees of a companion sitting placement service are generally treated as self-employed for all federal tax purposes. However, a sitter not affiliated with a companion sitting placement service may be considered to be an employee of the individual for whom the sitting is performed,
depending on whether the individual for whom the sitting is performed has the right to direct and control the sitter.